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Lord Rutherford: Manchester, 1907–19: a Partial Portrait

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A MEMORIAL LECTURE must necessarily be in part biographical, and biography, we are told, cannot avoid incursion into autobiography. You will forgive me, therefore, I am sure, if I speak of myself this afternoon as well as of my subject. I am not a physicist—not even a nuclear physicist—but an inorganic chemist, a former pupil and admirer of Lord Rutherford. I think I am the only one since their Montreal days who has worked with both Rutherford and Soddy, so, whatever else I am ignorant of, at least I should be acquainted with the great disintegration theory of radioactivity which these young men sprung on the learned, timid, rather unbelieving, and, as yet, unquantized, world of physics in 1902 and 1903. I don't intend, however, to take you today quite so far back into ancient history as that. I shall begin in 1907 and stop in 1919. That embraces the great middle period of Rutherford's life of discovery that followed the twelve years spent at Cambridge and Montreal, and preceded the eighteen years of his return to Cambridge till his death in 1937. The Manchester period, like the others, was a great period, perhaps the greatest, and it was almost certainly the happiest period of a particularly happy life.

Ernest Rutherford, his New Zealander wife, Mary Newton, and their six-year-old and only child, Eileen, settled in Manchester in a medium-sized, well-planned, admirably warmed house in Withington, on the main road to the South from the University. It was in this house that Professor and Mrs. Rutherford were hospitable hosts in a hospitable University. Supper in the white-painted dining room on Saturdays and Sundays preceded pow-wows till all hours in the study on the first floor; tea on Sundays in the drawing room often followed a spin on the Cheshire roads in the motor. Manchester in 1907 was the Manchester of the *Guardian* and the Hallé Concerts and of Miss Horniman's Repertory Company, where, among the younger members of the company, were Lewis Casson, not then knighted, and Sybil Thorndike, not yet 'Damed'; the Manchester of cotton, liberalism, Free Trade, and the Manchester school; the home of the Hopkinsons, Ramsbothams, Cleggs and Marsdens as well as of the scarcely less Lancastrian Behrens and Schusters, Simons and Zimmerns. At the University Tout and Tait were great names in history, Alexander in philosophy, Schuster in physics, Elliot Smith in anatomy and Perkin in chemistry. (It is interesting to note that in Perkin's laboratory in 1907 there was a young graduate destined, like Rutherford, to win the 1851 Exhibition

scholarship, to become a professor overseas before obtaining a chair at one of the older universities in England, to gain the Nobel Prize for Chemistry and the Copley Medal, and to become the President of the Royal Society—Sir Robert Robinson.) In that safe and easy world before the *débâcle* of 1914 prices were low. They had to be, for Universities and students were on the whole poor. A research student could then 'manage' at a University like Manchester on a bare hundred pounds a year. Stipends, except to those with very special qualifications, were, by today's standards, fantastic. Rutherford himself had £1,600 a year—a very high salary for those distant days. His regular staff in the department of physics, consisting of nine graduates, also had £1,600 a year—but divided between them—four at the bottom of the list having but £125 a year. You will be glad to know that all of these have had rises since, in more senses than one. One of the nine still remains on the Manchester Physics staff, one would have obtained the Nobel Prize for physics had he not been killed in the 1914–1919 war—H. G. J. Moseley—two became heads of Cambridge colleges and the remaining five professors.

Rutherford impressed me—an impressionable Scot from Glasgow—from the first even more by his kindness and generous outlook on life than by his undoubted great ability in physics. He was a man who never did dirty tricks. It was delightful to be in the daily company of one who could overlook trifles and not harp on real or imaginary grievances or failures. He had been brought up in New Zealand as a presbyterian and, although in his Manchester period he was no churchgoer, he had preserved in the serious part of his life the great puritan qualities. When relaxed or off duty he had, as you all know, a wonderful manner, the manner of one who always seemed to be in tearing spirits. His talk abounded in banter and slang, in wisecrack and epigram, in burlesque and misquotation. Strangers, not knowing the serious man he was, and meeting him away from worry and responsibility, might also gasp at his exuberance, and, certainly, if they were unaware of his other side, they would gain a wrong impression of the man. His loud laugh, his assertive, even boastful, manner at times; and the loud voice, were only parts of him. He had, as I have said, the best of the puritan qualities of heart: a clear, honest, simple integrity, steady composure in the face of difficulties, gentleness on occasion, intelligence, a slow and cautious way of reaching conclusions of importance, a habit of understatement, kindness of heart, decency, and profound and loyal affection for home, parents and pupils. This was undoubtedly the side of himself he showed to Nature when he was brooding over her secrets or describing what he had done in the scientific journals. He kept his mind instinctively on what was good and positive in the investigations he was making, and, no doubt, he was the better able to do this because he could let off steam, as it were, in moments when no critical person was present. He has been well described as a tribal leader by one of his biographers. That is very true. He could be aggressive, even hard, when his work, or that of his pupils, was being stymied, as he thought, by incompetence. But he was fundamentally fair and fundamentally humble. He hated pretentiousness with the derision of a Mark Twain. "The vanity of the man was just terrible", he would say, "I couldn't hear what the man was saying for looking at it." Or, again, of some nincompoop in high position (such were usually referred to as 'johnnies'): "That man is like the Euclidean point: he has position without magnitude." He seemed to have the personal qualities, as well as the gifts in

science, to enable a large band of devoted research workers continuously to adhere to him. And, despite this, in the Manchester days, he was no despot, not even a benevolent despot, as he has been described. He showed little envy or jealousy of the position or the work of others. When he got angry with anyone it was because they were interfering, not with his personal success, but merely with the good prospects of the cause. He was by no means unconscious of his greatness, but he had none of the common self-applause that exaggerates what is ordinary into something supreme, and sets down what is in fact good fortune to his own foresight and penetration. Rutherford had supremely foresight and penetration in addition to good fortune. He *was* fortunate, to be sure. He was fortunate in getting the 1851 Exhibition scholarship from New Zealand precisely at the time that x-rays were being discovered and in having J. J. Thomson at Cambridge as his mentor. It was fortunate, too, that radioactivity was such a simple subject. How admirable that it was atomic and not molecular, that the spontaneity of the disintegration was unaffected by any chemical or physical condition, that disintegration, wherever it occurred, followed one law only, that never more than one particle at a time was ejected by the disintegrating atom, and that altogether there were two kinds of particles only! He was fortunate always in his co-workers (and never more so, may I say, than when he was the Cavendish professor at Cambridge). But the basis of good fortune for him was not luck or chance. It resided, no doubt, in the times and the places where he was; but it derived supremely from the character and personality of the man himself and his intellectual gifts.

What were those gifts? His greatest gift was surely his insight into scientific problems. He always saw further ahead in his work in physics than any of his contemporaries and saw more deeply. He saw what was important and what trivial in ideas and results, so that neither time nor pains were lost in following roads that led nowhere. He had been brought up in the physical world of continuity, of induction, of waves, and of the mathematical theories then dominant. He had almost to make a clean break with this environment, almost to invent discontinuity, to imagine paradoxically that by a proper study of the smallest thing in nature, the atom, the main secrets of the physical universe would ultimately be disclosed. And in the study of the atom we now see how wise he was to concentrate on the α-particle and to regard as secondary the β-particle and the γ-wave.

His other great gift was to design experiments that asked of Nature the most pertinent questions and then to brood for long over the answers. In this respect he was of the great company of Newton and Faraday. They knew what to ask and how to pay attention not so much to what Nature was saying as to what Nature was whispering. In this Rutherford was an artist. All his experiments had style. Let me illustrate: One of the early experiments he did at Manchester was with Royds on the identification of the α-particle with the atom of helium. He had known for years that the α-particle was likely to be the helium atom, but he had to make assurance doubly sure. A glass tube blown so thin that it allowed the α-particles easily to penetrate its walls was shown to be gas-tight. Filled with radon it was surrounded by a second glass tube highly evacuated. In this tube it was simple to show that helium accumulated with the passage of time as it got filled by the particles entering it. Then, in 1908, how beautiful, as well as how accurate, was Rutherford's determination of Avogadro's number!

He counted accurately the number of α-particles emitted in a given time by a known mass of radium and determined also the value of the charges the particles were carrying. From these data he obtained a value of Avogadro's number which was forty per cent different from the best of earlier determinations but which is still within three per cent of the best determinations of today. Or again, think of the simplicity of the device developed by Geiger and himself to register a single α-particle. A wire charged almost to breaking potential and connected to an electrometer was inserted in a tube into which a very small stream of α-particles was allowed to enter. As one particle entered, its feeble ionization, increased greatly by the ionization from collision, sufficed to cause a discharge easily registered by an electrometer. Or think of the work on the scattering of α-particles by thin films of metal where the number scattered though a given angle was counted by well-rested eyes in a dark room by the flashes which each one individually gave on a screen of zinc sulphide; or the comparison of two very disparate standards of γ-radiation by putting each in turn on an optical bench at such distances from a measuring instrument that a constant result was recorded, and then invoking the inverse square law for the calculation. On a backward view one saw the beauty of the method of investigation as well as the ease with which the truth was arrived at. The minimum of fuss went with the minimum chance of error. With one movement from afar Rutherford, so to speak, threaded the needle first time.

Rutherford's Manchester work has often been described and will be merely summarized now. It comprised a wide study of α-particles till about 1911, then an investigation of the scattering of α-particles by metallic screens which led to the enunciation of the great nuclear theory of the atom in 1913, and, thirdly, the work begun in 1913, but much interrupted by the war, which culminated in the successful disintegration of the nucleus of nitrogen in 1917. There was an admirable description of the co-operation between Rutherford and his pupils in Dr. Marsden's lecture last year. Rutherford was always the creator of ideas and the main driving force, but while he made the fullest use of their willing help he never 'ran' his pupils or played the dictator, even a benevolent one. It was a reasonably free community. Geiger, Boyle, Boltwood, Bohr, Fajans, Hevesy, Gray and Andrade were among the more notable arrivals in the laboratory from other Universities. Russ, Makower, Chadwick, Darwin, Marsden, Nuttall, Robinson and Moseley were among those on the regular staff. Of these, Professor Robinson and Dr. Marsden have already given a Rutherford Memorial lecture to you. Sir James Chadwick would have been in my place this afternoon had he not unfortunately become ill, and Sir Charles Darwin, I am glad to see, is with us now.

Moseley from the first was recognized by his colleagues as the most original and gifted on the regular staff after the professor himself. He was a nice man but not 'hail-fellow-well-met'. He was an Etonian not at all amiable to fools and time wasters. He rarely let any loose statement pass in conversation without either a total denial of its validity or a considerable and often pungent modification of the original formulation. He was one of the few who contradicted Rutherford. He worked by choice towards the end of his time mainly through the night, and was one of the hardest workers the laboratory had ever had. Geiger was too much of an Olympian for me to know well. Gentle, without being docile, and aloof, he seemed in laboratory hours to live entirely for the work. He was a beautiful

experimenter of the Sir James Dewar type, splendid with his hands. Like many Germans, he loved good music and good dinners. The four young demonstrators who were native to the laboratory, Marsden, Chadwick, Robinson and Nuttall, had two things in common, devotion to work and a high sense of humour. They were, moreover, quite content with the meagre stipends which the University paid to them. Bohr was one of a small group who advised on mathematical theory as well as carrying out their own research work. His coming to Manchester just at the right time to give Rutherford the maximum help on the mathematical side of the nuclear theory of the atom was indeed providential. Bohr came to England from Denmark in 1912 to work at Cambridge, and at Cambridge he might have stayed out his time had he felt he fitted in there. A chance visit to Rutherford weakened his original intention. He felt instinctively he could fit in better with him than at Cambridge. When Bohr dallied with the idea of coming to Manchester Rutherford persuaded him not to alter his original plan too precipitately. "Stay in Cambridge as long as you can", said Rutherford in effect. "It's a good place and there's plenty going forward there. You'll like it the better the longer you are there. And, in any case, Manchester is always here. It won't run away." Almost the next thing we heard, however, was that Dr. and Mrs. Bohr had settled in Manchester, and the rest of the story: how Bohr co-operated on the nuclear theory of the atom and rescued the Periodic Classification of the elements from the curves and spirals and whatnots in which it had got unfortunately embedded, is it not one of the best known pieces of history in science?

Here I may interpose a few stories, characteristic rather than funny, to illustrate the man. Rutherford loved chaffing his younger research workers on occasion at tea-time in his laboratory. As I was the only Scot amongst them I came in for a good deal of chaff on the real or supposed foibles of Scotsmen. He thought them an over-scholarshipped and over-praised lot. "You young fellows come down here from across the border with such testimonials written by your Scots professors that, why man alive!, if Faraday or Clerk Maxwell were competing against you they wouldn't even get on to the short list." One day he told us he had picked up a delightful phrase from one of the novels of H. G. Wells: "a fellow of the Royal Society in the sight of God", and thereafter, on occasion, the young Scotsman of science was not only, on paper, miles better than Maxwell and Faraday, "but already at twenty-four a fellow of the Royal Society in the sight of God". I once saw Rutherford genuinely surprised. We had been out on a laboratory visit to a works where one of the products was a plated glass teapot. (These were quite popular at one time.) The inner piece of glass held the warm tea, the outer faced the world. Between was deposited some white metal which shone brightly. It was as though a glass mirror had been fashioned into a teapot. To make polite conversation Rutherford asked the man showing him the teapot what metal was used for the plating. He was quite staggered when the man replied "Platinum". Platinum in those days was very rare and never spoken lightly of. Moreover, it happened that just at that time Rutherford had shown that what afterwards was called the nucleus of platinum had a charge of about one hundred positive units. Rutherford was consequently emotionally interested in platinum, and so expressed his incredulity about the answer given in a loud and sustained "Wh-a-a-at?". He wasn't going to be fobbed off with sales talk or have his leg even lightly pulled. "Platinum?" repeated Rutherford, "Platinum? Platinum?" "Yes", quietly answered the man, almost apologizing

for the word. "This isn't a case of 'only the best being good enough' for these teapots. It's a case of the most expensive being the cheapest", and he started talking of thinness of films and coverage power and details of that sort. "But do you really mean platinum?", asked Rutherford again, giving the man one more chance to withdraw. "Oh, yes", said the man, quite cheerfully. "It's platinum all right", and then to bring it right down to the level of the Nobel Prizeman in Chemistry, he added: "one of the osmium, iridium family of metals", and then, turning to me to clinch the matter, he said, "atomic weight 195·2." The moment he said that, I knew, somehow, that it was platinum. Platinum, in fact, it really was. Rutherford, genuinely surprised but not yet defeated, then retaliated by asking how much was the cost of plating a single teapot. All he evidently wanted to know was whether it was five shillings, one shilling or what. It was clear from the way the question was received by the man that we were in for a long *viva*. "Grade A or grade B?", he asked. Rutherford, at a venture, murmured rather boredly "B". "Grade A is better", he was encouraged to believe. "All right then", roared Rutherford, "grade A". "We don't actually quote for single teapots", resumed the conscientious man. "I'll quote you the fiftieth of the cost of fifty." "All right", shouted Rutherford, whose patience had almost given out. "Wholesale or retail?", continued the exasperating man, and there would have been a scene had not the answer to Rutherford's "wholesale" put everyone in high good humour. For the answer that came at long last, given calmly and weightedly, as though empires depended upon it, was, believe it or not, twopence three-farthings! I can still hear Rutherford's long and loud laugh as he heard the unexpected news, and for some time afterwards he had a new story to work off on his friends.

May I give one more story, not funny, not even very complimentary to Rutherford himself, but characteristic of his boisterous manner to strangers, the antithesis, as I have said, of his working and brooding manner? One day at a formal luncheon a bishop started to tell me a story of how he had met my professor at an earlier meal. Knowing that Rutherford was a New Zealander, he had asked him how many people there were in the South Island. He had been quite genuinely surprised to learn in answer that it was only about 250,000. He had imagined till then that the population was of the order of three or four millions. To indicate his surprise, and to get confirmation of the smallness of his figure, he compared it to Rutherford with the population of an English town. "As I spoke to him of this", continued the Bishop to me, "I saw your professor's face flush. You could almost see the blood flowing up the neck and flooding the face....". Just at that interesting point the chairman at the luncheon proposed the health of the King. We rose, and I never heard the end of the story—at least from the bishop. A few days later, however, as I arrived a little late for the laboratory tea, I came in at the professor's words: "....bishop in gaiters. It was perfectly ludicrous. He thought there ought to be about four millions there. 'Quarter of a million?', he said to me incredulously. 'Do you mean to say there are only 250,000 there? Only about the population of Stoke-on-Trent?'" It was then that I realized why Rutherford had got excited in the bishop's story. The idea of comparing his lovely South Island with some place in England like Stoke-on-Trent! So I waited for the conclusion of the bishop's story. And it came. "So I said to him", continued Rutherford, and then he paused and looked kindly at us all. "I hope there are none of you here from Stoke-on-Trent. So I said to him: 'Maybe the population is only about that of Stoke-on-Trent.

But let me tell you, sir, that every single man in the South Island of New Zealand could eat up the whole population of Stoke-on-Trent, every day, before breakfast, and still be hungry'."

Rutherford loved pungent phrases and liked to use them in talk. He did not pretend to originate them. He was content to pass them on. I have mentioned already the wheeze about the Euclidean point and Wells's gibe about the young F.R.S. in the sight of God. Phrases like 'a mere flea in the ocean', 'trembling like an aspic', 'keeping your nose to the gridiron', 'Athens the crater of civilization' were constantly interlarded into conversation, and he could use them with great effect whenever he wanted to. (These are not actually his. I have borrowed them to illustrate.)

I now raise the question with you: Why were the inorganic chemists so slow in the years immediately preceding 1914 in arriving at the conceptions of isotopes and atomic number? When we realise the importance of these conceptions in the nuclear physics of today, as well as in inorganic chemistry, we cannot but criticize the casual manner in which the earlier chemists eventually arrived at them. Crookes was the first to put forward the idea that developed later into that of isotopes. In 1886 he formulated his suggestion of meta-elements. He imagined that an element such as iodine might have atomic masses other than that of 127. The most prevalent mass in Nature would be 127. There would be an appreciable concentration, however, of masses of, say, 126 and 128, smaller concentrations of masses of 125 and 129, and so on. These deviations from 127 would not suffice to make an appreciable difference in the ordinary chemical reactions of the different masses. They would reveal themselves, however, in certain physical properties such as spectra. Thus the different iodine atoms would be 'non-separable' chemically (to use the phrase of 1910), but with regard to the seven series of bands in the absorption spectrum of iodine Crookes imagined that "some of these molecules may emit some of the series, others others, and in the jumble of all these molecules, to which the name 'iodine vapour' is given, the whole seven series are contributors". That certainly was an idea, an idea well worthy of a great chemist. Crookes, indeed, was a kind of Rutherford of chemistry but a solitary worker, entirely without the 'tribal leadership' qualities.

The curtain descended on this novel theory for twenty years. It rose again in 1906. In that year Otto Hahn discovered a new product, radio-thorium, in the thorium disintegration series, and later found that although it differed from thorium by 4 in atomic mass it could not be separated from it by any chemical reaction to which it had been put. In 1907 McCoy and Ross confirmed this 'non-separability', as it began to be called. In 1908 Boltwood found that uranium differed from every other known radio-element in expelling on disintegration not one, but two α-particles. It was concluded, in consequence, that ordinary uranium consisted of two uraniums, each expelling a single α-particle on disintegration, although it was not then known by how much the two differed in atomic mass. In 1909 Strömholm and Svedberg found that radium, thorium X and actinium X were non-separable, and in the next year Soddy, and independently Marckwald, found that mesothorium 1 and radium were also non-separable, a result, it appeared, that Hahn had himself known for some years. The work of Keetman in 1909, however, turned out to be of most consequence. In finding that ionium and thorium, which were known to differ in atomic mass by 2, were non-separable he had gone 'all out' to effect a chemical separation. The other

workers had contented themselves with showing that their non-separable pairs of radio-elements were extremely similar. Keetman tried every chemical and physical device that was available before he had to confess himself defeated. Moreover, in all the other cases the concentration of one of the non-separable radio-elements was known from its half-value period to be below what is called 'weighable amount'. In Keetman's preparation, on the other hand, ionium was present to the extent of about 1 per cent. The excuse that non-separability was due simply to adsorption of a vanishingly small concentration of a radio product on a compound similar to but not necessarily identical with it could no longer be urged. Keetman made it quite clear that non-separability was not just an extreme case of 'difficulty of separation', but something probably fundamental. This was confirmed by Rossi and myself in Rutherford's laboratory. We were given a preparation of thorium that contained at least 2 per cent of ionium, if the half-value of ionium then accepted (and since confirmed) were not many times smaller than was thought. We took the opposite view to that of Crookes. He had imagined that chemical non-separability would be revealed by differences in spectra. We imagined that there would be no difference whatever in the arc spectra of ionium and thorium. Rossi, who was an experienced spectroscopist, was unable to find the slightest difference between the arc spectrum of pure thorium and the mixed spectra of thorium and ionium in conditions when the presence of one quarter of one per cent of impurity would have been easily detected.

With the fact of non-separability, with about forty radio-elements somehow to be 'explained' or fitted into the Periodic Table, and, as we now know, only ten places above the position of lead available, it must strike you as odd that the chemist hesitated for so long to distribute the radio-elements in the available places of the Table. That would have given us at once the idea of isotopes. It would have given us also the displacement laws, and from the displacement laws it would have been seen that the number of positive charges carried by an atom was more important than its mere atomic mass. Note that it would not have given us the absolute values of the atomic numbers of thorium and uranium; that had to wait for the work of Moseley and of Bohr, but it would have given us the atomic numbers of all the radio-elements relative to that of one of them arbitrarily chosen—and this as early as 1911, a year before Rutherford and his co-workers were evolving the idea of atomic numbers from their experiments on the scattering of α-particles by elements like gold and platinum, and two years before Moseley's classical work on the X-ray spectra of the elements. In defence of his apparent lack of insight, or even courage, the chemist could have advanced two points. He could argue that it is unwise to erect into a principle the mere fact that some analytical chemists had failed to effect certain separations. Inability to do something that seemingly ought to be done is surely better met with "the more fool, you" retort than with the acceptance of a new principle. He could argue also that in 1911 you could not, in fact, 'trust' the Periodic Classification. As a classification it was obviously not periodic. The rare-earth elements demonstrably did not fit in. There were difficulties over the atomic weights of argon and potassium and other pairs of adjacent elements and, worst of all, there was no criterion for limiting the numbers of elements that might be heavier than lead or lighter than hydrogen.

The real difficulty with the inorganic chemist in that period, however, was not that Mendeléef's periodic classification in its development had never kept pace with discovery (so that it always appeared to critical minds more a help to the student or a mnemonic for the memorizer than a true principle in embryo), but that the climate of opinion in inorganic chemistry then was adverse to any kind of speculation or even theorizing. Chemistry, we were always being told, was an experimental science. No good ever came from pontificating on the ways of Nature from the comfort of an armchair. The laboratory bench, not the sofa, we were sarcastically told, was where the truth would be found. And so no inorganic chemist of eminence, not Ramsay, Crookes, Mme. Curie, Soddy, Hahn, Marckwald, or Welsbach, took the final and decisive step in 1911. In the previous year Soddy in comparing a radio-element with its parent expelling an α-particle fastened on the idea of valency. Uranium in expelling an α-particle dropped its valency from 6 to 4; thorium in doing the same dropped its valency from 4 to 2; radium in producing radon dropped its valency from 2 to 0. Valency was the property insisted on. Position, now so simple and obvious an idea, was not then thought of.

I end by speaking very briefly of a point, raised by any consideration of the life of Lord Rutherford, which has not been much discussed by those who have preceded me in addressing you. The point is the paramount importance of the great man in science. I believe from the bottom of my heart two things in this connection. One is that we cannot afford in science not to know anything that possibly can be discovered. Knowledge has no doubt a bad side, but its credit is enormously greater than its debit in a decent world; life on the whole is enriched by it. The other is that in the pursuit of knowledge we cannot afford to do without the great man. Rutherford often said in his modest way that men of science are not dependent on the ideas of a single man, but on the combined wisdom of thousands of men, all thinking of the same problem, and each doing his part in adding to the great structure of knowledge going up. In some sciences, and in the practical applications of scientific knowledge, the statement is probably truer than most of us realize. But is it altogether true of a fundamental science like physics? Surely it is nearer the mark to say that the more fundamental the science the greater is the need of the big advances which only great men can make. At the least they save us years of waiting while the team of talented workers, however well organized, make their belated discovery. And there are cases, I assert, where if the great man does not do his work the darkness remains permanently unpierced. Where should we be today in physics if Rutherford had not lived among us and given generously of his great endowment? By probing the atom to its very depth he not only revealed great truth and great beauty; he showed us by example what one man can do when he makes the most of his great gifts. His life, in Meredith's phrase, may have been "a little holding", but it was "lent to do a mighty work". That such as he have lived among us must raise our hopes of man's worth and dignity in these dark days.

The Nuclear Surface Energy

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ABSTRACT. The kinetic and potential parts of the nuclear surface energy are calculated on the basis of the statistical model of the nucleus taken to first order and using a gaussian interaction between particles. The resulting surface energy is found to be of the right order of magnitude, the calculated figure being in fact 55% of the empirical value.

§1. INTRODUCTION

THERE are at present no satisfactory calculations of the nuclear surface energy, although the empirical value of about 61 MeV/barn is well established. The earliest calculations by v. Weizsäcker (1935) treat only part of the effect. Bethe and Bacher (1936) pointed out that v. Weizsäcker's treatment was not valid and made a crude calculation which gave about one-fifth of the observed energy. Feenberg (1941) believed to have obtained results of the right magnitude, but his calculations are erroneous (see §5).

The surface energy arises from the fact that near the surface both the kinetic and potential energies are different from their values inside a large uniform mass of nuclear matter. First, both depend on the particle density, which within the surface layer is less than the bulk density; this leads to a reduction in the magnitudes of both the kinetic and the potential energy densities, the net result being a diminished binding since the bulk density corresponds to an optimum. These effects are present already if one regards the energy density at each point merely as a function of the particle density at that point, using the relation that would hold for uniform density. This is the treatment used by Bethe and Bacher (1936). In addition, however, there are effects specifically due to the fact that the density is not uniform. In the potential energy this gives rise to the same situation as in the classical theory of surface tension and is connected with the fact that a particle near the surface has only half the normal number of neighbours. In the kinetic energy the variation of density contributes an increase which is to be expected from the uncertainty principle.

A systematic treatment of all these effects is possible using the statistical model of the nucleus. In the orthodox statistical treatment the properties of nuclear matter are investigated by imagining a large potential well filled with a mixture of neutrons and protons at the required density, and calculating the energy per unit volume of such a system for points not too close to the surface of the well. This gives the volume part of the nuclear binding. All that is required to obtain the surface energy is to carry out an analogous calculation in the surface region of the well. This will be done in the present paper.

§2. CALCULATION OF THE SURFACE ENERGY

We disregard the effect of curvature of the nuclear surface and consider therefore an assembly of particles bounded on one side by a plane. The plane can be thought of as one face of a large cube, the potential being zero inside and infinite outside the cube. (A gradually rising potential will be treated later.)

With the origin of coordinates in the plane and the x-axis along the normal, the wave function of a particle of momentum $\mathbf{p}=(p_x, p_y, p_z)$ can be written as

$$\psi_{\mathbf{p}}=\psi_x\psi_y\psi_z$$
$$=(2/L)^{1/2}\sin(xp_x/\hbar)\,.\,L^{-1/2}\exp(iyp_y/\hbar)\,.\,L^{-1/2}\exp(izp_z/\hbar)\quad\ldots\ldots(1)$$

where $L^3=$ volume of the cube.

As usual, we have replaced the boundaries in the y and z directions by a condition of periodicity, but since we wish to study the neighbourhood of the surface $x=0$, we must use the correct boundary condition at that surface. In the x-direction we are therefore dealing with standing waves described by a quantity p_x whose sign we take as positive. This means that in momentum space the occupied states fill a hemisphere (radius P, say) at a density $4L^3/h^3$ if two particles are allowed per state. (We are for the moment considering only one kind of particle, for example, neutrons.) The density of particles as a function of x is then

$$n(x)=\sum_{\mathbf{p}}\psi_{\mathbf{p}}^*\psi_{\mathbf{p}}=(4L^3/h^3)\iiint\psi_{\mathbf{p}}^*\psi_{\mathbf{p}}$$
$$=(8/h^3)\iiint\sin^2(xp_x/\hbar)$$
$$=n(\infty)\{1+(3\cos X)/X^2-(3\sin X)/X^3\},\qquad\ldots\ldots(2)$$

where $X=4\pi x/\lambda_0$, $\lambda_0/2\pi=\hbar/P$, $n(\infty)=P^3/3\pi^2\hbar^3$ (see Figure 1). It is seen that

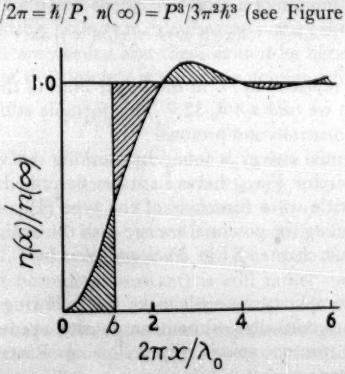

Figure 1. Particle density as function of distance. The position of the effective surface is indicated. The areas in the two different shadings are equal.

the density drops appreciably before the surface $x=0$ has been reached, the reason being that the uncertainty principle makes a sudden change in density energetically unfavourable. It is therefore reasonable to think of the surface of the nucleus as located not at the edge of the potential well but at some distance within the region of falling density. We shall find it convenient to define the 'effective surface' as that surface which would contain the correct total number of particles if the density were equal to the bulk density within the surface and zero outside it. The distance of this effective surface from the edge of the well is

$$b=\int_0^\infty\{1-n(x)/n(\infty)\}\,dx.\qquad\ldots\ldots(3)$$

This means that the differently shaded areas in Figure 1 are equal.

To find the kinetic energy density we calculate†

$$t(x)=\sum_{\mathfrak{p}}\psi_{\mathfrak{p}}{}^{*}\left(-\frac{\hbar^2}{2M}\nabla^2\right)\psi_{\mathfrak{p}}$$
$$=t(\infty)\{1+(5\cos X)/X^2-(15\sin X)/X^3-(30\cos X)/X^4+(30\sin X)/X^5\}, \quad \ldots\ldots(4)$$

where $t(\infty)=P^5/10\pi^2M\hbar^3$ and M is the nucleon mass. From $n(x)$ and $t(x)$ we can calculate the surface kinetic energy in the following way: consider the nuclear matter inside a uniform prism erected along the normal on unit area of the $x=0$ surface. Consider a portion A of the prism extending from $x=0$ to $x=x_1$ ($x_1\gg\lambda_0/2\pi$) and a second portion B well away from the surface and of length l such that A and B contain the same amount of nuclear matter, viz: $ln(\infty)=\int_0^{x_1}n(x)\,dx$. The kinetic energies associated with A and B are $\int_0^{x_1}t(x)\,dx$ and $lt(\infty)$, respectively. Any difference will be due to the presence of the surface in the case of A. Hence the surface kinetic energy excess per unit area is

$$\int_0^{x_1}t(x)\,dx-lt(\infty)=\int_0^{x_1}\{t(x)-t(\infty)n(x)/n(\infty)\}\,dx\simeq t(\infty)x_t,$$

where
$$x_t=\int_0^{\infty}\{t(x)/t(\infty)-n(x)/n(\infty)\}\,dx. \quad \ldots\ldots(4a)$$

(x_1 can obviously be replaced by ∞ in the upper limit of the integral.)

Using (2) and (4) we find $x_t=\lambda_0/32$. This formula still holds for a mixture of equal numbers of neutrons and protons.

The surface potential energy is found by working out the expectation value of an interaction operator $V(x_{12})$ between states described by antisymmetrized products of one-particle wave functions of the type (1). For a description of the method of calculating the potential energy with the ordinary statistical model the reader may consult chapter XI in *Nuclear Forces* by L. Rosenfeld (in future referred to as N.F.).

For the sake of simplicity we shall make the following assumptions, which do not affect the result critically: (i) neutron density = proton density; (ii) total neutron spin = total proton spin; (iii) following Rosenfeld we assume a symmetrical interaction

$$V(\mathbf{r}_{12})=J(\mathbf{r}_{12})(\boldsymbol{\tau}^{(1)}\cdot\boldsymbol{\tau}^{(2)})\{a_\tau+a_{\sigma\tau}(\boldsymbol{\sigma}^{(1)}\cdot\boldsymbol{\sigma}^{(2)})\}$$

in the notation of N.F.

The potential energy density (defined as a positive quantity) as a function of $\mathbf{r}_1$ is then

$$v(\mathbf{r}_1)=\tfrac{3}{2}(a_\tau+3a_{\sigma\tau})\cdot\int|n(\mathbf{r}_1,\mathbf{r}_2)|^2J(\mathbf{r}_{12})\,d\tau_2 \quad \ldots\ldots(6)$$

(cf. N.F. Ch. XI, equation 24), where $n(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\mathfrak{p}}\psi_{\mathfrak{p}}{}^{*}(\mathbf{r}_1)\psi_{\mathfrak{p}}(\mathbf{r}_2)$ is the 'mixed density' of one kind of particle, and the integration extends over all positions of particle (2).

† A small point arises in connection with the two possible definitions of the kinetic energy density as $\sim\Sigma\psi^*\nabla^2\psi$ or $\sim\Sigma(\text{grad }\psi)^2$. It can be shown that although the form of $t(x)$ is different in the two cases, the surface energy as given by (4*a*) (see below) is the same in both.

For the conventional statistical model $v(\mathbf{r}_1)$ is a constant in space, which we denote by $v(\infty)$. For instance, for a gaussian interaction $J(\mathbf{r}_{12}) = C\exp[-(r_{12}/a)^2]$ the following result is well known:

$$v(\infty) = \tfrac{3}{2}(a_\tau + 3a_{\sigma\tau})\,.\,(2/3\pi^{5/2})(2\omega_0)^3 f(2\omega_0),$$

where
$$f(y) = 2/y^3 - 3/y + (1/y - 2/y^3)\exp(-y^2) + \sqrt{\pi}\,\mathrm{erf}\,y,$$
$$2\omega_0 = 2\pi a/\lambda_0.$$

In our case the energy density $v(\mathbf{r}_1)$ is a function of the distance from the surface. Inserting the wave functions (1) in (6) we can calculate $v(x)/v(\infty)$ explicitly (see § 6). The calculations are lengthy, but the final graph is qualitatively similar to $n(x)/n(\infty)$.

In analogy with the kinetic energy excess $t(\infty)x_t$ we can define a potential energy deficiency per unit area by $v(\infty)x_v$, where

$$x_v = \int_0^\infty \{n(x)/n(\infty) - v(x)/v(\infty)\}\,dx.$$

Before giving the results of these calculations we shall generalize the above procedure to the case when the potential at the edge of the potential well rises gradually instead of becoming infinite at $x=0$. Ideally we should now introduce a general function $V(x)$ describing the potential at the edge of the well and vary it until the associated surface energy becomes a minimum. Such a variational procedure is impracticable because to calculate the surface energy explicit solutions of the wave equation are needed and these cannot be obtained except in a few simple cases. One of the simplest is a linear potential defined as follows:

$$V(x) = \begin{cases} 0 & \text{for } x>0, \\ -V_0 x/x_0 & \text{for } x<0. \end{cases}$$

We take V_0 to be $P^2/2M$. The reciprocal of x_0 is then a measure of the gradient of the potential. An estimate of the surface energy can then be obtained by minimization with respect to x_0. This estimate will, in fact, be an upper limit on the value which would be obtained by a variational calculation with an unrestricted form of $V(x)$. It might be thought that the fact that $V\to\infty$ as $x\to-\infty$ (instead of becoming constant) is still rather unrealistic, but in fact the precise behaviour of $V(x)$ for large and negative x is unimportant as all the wave functions there have been damped out exponentially.

The solution of the wave equation in the new potential $V(x)$ can again be factorized into $\psi_x\psi_y\psi_z$. The components ψ_y, ψ_z remain as before, but ψ_x for $x<0$ is now expressible in terms of Bessel functions. It is easily verified that in place of $\sin(xp_x/\hbar)$ we have

$$q(\theta,\chi) = \begin{cases} \dfrac{\sin\Delta(\theta^2)}{U(\theta^2)}\,.\,U(\chi+\theta^2) & \text{for} \quad \chi<0, \\ \sin[\tfrac{3}{2}\theta\chi + \Delta(\theta^2)] & \text{for} \quad \chi>0, \end{cases}$$

where
$$\chi = (2\lambda_0/9\pi x_0)^{1/3}(2\pi x/\lambda_0),$$
$$\theta = (4\pi x_0/3\lambda_0)^{1/3}(p_\infty/P),$$
$$p_\infty = x\text{-component of momentum for } x>0,$$
$$\Delta(\theta^2) = \arctan[3\theta U(\theta^2)/2U^1(\theta^2)],$$

and
$$U(\epsilon) = \begin{cases} \epsilon^{1/2}[J_{1/3}(\epsilon^{3/2}) + J_{-1/3}(\epsilon^{3/2})]/\sqrt{3} & \text{for} \quad \epsilon>0, \\ (-\epsilon)^{1/2}K_{1/3}((-\epsilon)^{3/2})/\pi & \text{for} \quad \epsilon<0, \end{cases}$$

where $J_{1/3}$, $K_{1/3}$ are Bessel functions and $U' \equiv dU/d\epsilon$. The function ψ_x $(=\sqrt{(2/L)}q)$ is normalized so that

$$\int_{-\infty}^{L} |\psi_x|^2\, dx \to 1 \qquad \text{as} \qquad L \to \infty.$$

In momentum space the states as labelled by p_∞, p_y, p_z again fill a hemisphere at the same density as before. It can then be shown (§ 6) that $n(x)$, $t(x)$, $v(x)$ are given by

$$n(x)/n(\infty) = 3\int_0^1 (1-S^2)q^2(\theta_0 S, \chi)\, dS. \qquad \ldots\ldots(8)$$

$$t(x)/t(\infty) = 5\int_0^1 \{\tfrac{1}{2}(1-S^4) - (V/V_0)(1-S^2)\}q^2(\theta_0 S, \chi)\, dS. \qquad \ldots\ldots(9)$$

$$v(x)/v(\infty) = (6/\pi^{1/2}\omega_0{}^2 f(2\omega_0)) \int_{-\infty}^{\infty} d(2\pi x'/\lambda_0) \exp[-(x'-x)^2/a^2]$$
$$\times \sum_{m=0}^{\infty} \left[\int_0^1 C^{(m)}(\omega_0{}^2(1-S^2))q(\theta_0 S, \chi)q(\theta_0 S, \chi')\, dS\right]^2, \qquad \ldots\ldots(10)$$

where $\theta_0 = (4\pi x_0/3\lambda_0)^{1/3}$, $\chi' = (2\lambda_0/9\pi x_0)^{1/3}(2\pi x'/\lambda_0)$,

$$C^{(m)}(y) = \frac{1}{m!}\int_0^y t^m e^{-t}\, dt.$$

It is easily verified that on putting $q(\theta, \chi) \to \sin^3\theta\chi = \sin(xp_\infty/\hbar)$ equations (8) and (9) reduce to (2) and (4). Also for $2\pi x \gg \lambda_0$ equation (10) can be shown to give $v(x)/v(\infty) = 1$.

Equations (8) to (10) were calculated by numerical integration. This is particularly laborious in the case of (10). No adequate approximate methods of treating the above expressions analytically could be found. In particular the Bessel functions in $q(\theta, \chi)$ must not be replaced by their 'W.K.B.' approximations, because in the surface region we are in the neighbourhood of the classical turning points of the particles at which the W.K.B. approximation is known to break down.

From (8), (9) and (10) the quantities x_t, x_v were calculated according to the formula

$$x_t = \int_{-\infty}^{\infty} \{t(x)/t(\infty) - n(x)/n(\infty)\}\, dx,$$

and the corresponding expression for x_v. (The lower limit of the integral is now $-\infty$ instead of 0.) Expressed in units of $\lambda_0(2\pi x_t/\lambda_0 = \zeta_t, 2\pi x_v/\lambda_0 = \zeta_v, 2\pi x_0/\lambda_0 = \zeta_0)$ they are plotted as functions of ζ_0 in Figure 2. The range a of the gaussian interaction assumed in the calculation of ζ_v was such that $\omega_0 = \pi a/\lambda_0 = 1{\cdot}00$. Since $\lambda_0/2\pi = 2R_0/(9\pi)^{1/3}$, where R_0 = nuclear radius constant $= 1{\cdot}42 \times 10^{-13}$ cm. this corresponds to a value of $a = 1{\cdot}86 \times 10^{-13}$ cm. which is approximately the current value of this quantity (cf. N.F. p. 153, table 7.13).

§ 3. COMPARISON WITH THE EMPIRICAL SURFACE ENERGY

We are now in a position to calculate the total surface energy and compare it with the surface term in the empirical binding energy formula which we take in the form: $E = E_{\text{vol}} + E_{\text{surf}} = -14{\cdot}66 + 15{\cdot}4A^{-1/3}$ Mev. per particle, where A = mass number (cf. N.F. p. 24, equation 4—since our calculation of the surface energy refers to an equal mixture of neutrons and protons without electrostatic interaction we have put $N = Z$, and omitted the last term in the formula quoted).

To make the comparison as nearly independent of the interaction strength C as possible we shall take the ratio $\eta = A^{1/3}E_{\text{surf}}/(-E_{\text{vol}})$. Thus $\eta_{\text{exp}} = 1{\cdot}05$. On the other hand the calculated energies are:

$$E_{\text{surf}} = 4\pi R_0^2 A^{-1/3}[t(\infty)x_t + v(\infty)x_v], \qquad E_{\text{vol}} = (4/3)\pi R_0^3[t(\infty) - v(\infty)],$$

therefore

$$\eta = 2(3/\pi)^{1/3}[\gamma\zeta_t + (1+\gamma)\zeta_v],$$

where $\gamma = t(\infty)/[v(\infty) - t(\infty)]$ is the magnitude of the ratio of kinetic to binding energy in a nucleus. The value of γ is known to be about unity. Explicit calculations based on the conventional statistical model with 'adjusted constants'* give 0·974 and 1·424 in first and second order calculations respectively. Taking the latter figure (the results are not sensitive to the value of γ chosen) we have plotted η as a function of ζ_0 in Figure 3. It is seen that the surface energy is least when $\zeta_0 \sim 1{\cdot}0$. The corresponding value of η_{min} is 0·58, which is 55% of the observed figure.

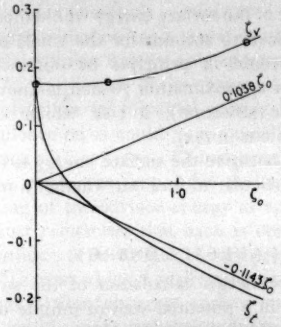

Figure 2. The kinetic and potential surface energies as functions of the inverse of the slope of the potential across the surface. See § 7 for the meaning of the straight lines.

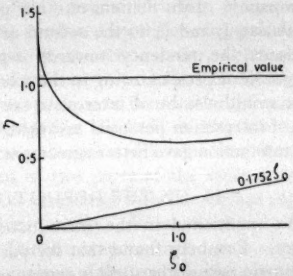

Figure 3. Total surface energy as function of the inverse of the slope of the potential across the surface. The straight line corresponds to the asymptotic case treated in § 7.

§ 4. DISCUSSION OF RESULTS

The functions ζ_t and ζ_v derived above are based on a first order perturbation calculation. Now it is well known that the statistical model taken to first order is not a good model of the nucleus. Thus with C and a derived from data on light nuclei the first approximation is known to give about 13% and the second 38% of the observed binding energy for a heavy nucleus. One might think, therefore, that a calculation which in first order gave 55% of the observed surface energy was in unexpectedly good agreement with experiment. We wish to point out that an agreement substantially better than for binding energy calculations is to be expected for the following reason. In our calculation of η the statistical treatment was invoked twice, firstly in the derivation of ζ_t and ζ_v and secondly in estimating γ. In the first case the quantities calculated are effectively ratios of surface to volume energies, and therefore independent of C

* C and a adjusted at each order of approximation so as to give the observed nuclear density and binding energy, cf. Swiatecki (1950).

(compare the binding energy calculations which are very sensitive to C). Unless there are reasons why the first approximation should be better or worse at the surface than inside the nucleus these ratios will be more reliable than the absolute values of the surface or volume energies calculated separately. As regards γ, its value, which depends implicitly on C, need not be known very accurately. For instance if the kinetic energy of a nucleus were twice that predicted by a first order calculation ($\gamma=2{\cdot}0$) the value of $\eta_{\min}$ would only increase to 0·66.

It can also be shown that no reasonable change in a will increase η to the observed figure. Finally an examination of the uncertainties involved in $\eta_{\exp}$ shows that unless the interpretation of the empirical binding energy is at fault, the value of $\eta_{\exp}$ should be accurate to about $\pm 10\%$.

There remains, therefore, a discrepancy which is probably significant. An explanation might perhaps be given in terms of the tendency towards α-particle clustering which is known to be present to some extent in nuclei. If this tendency (which makes for stronger binding) were jeopardized by the presence of a field of force in the surface region, the relative size of the surface energy would increase. This effect would have to be very pronounced to account for the whole of the discrepancy. Information on this point could in principle be obtained by calculating ζ_t and ζ_v to the second order of approximation (which is known to represent the tendency towards α-particle structure), a task which seems impossible at present owing to the complications in $v(x)$.

It would also be of interest to see how sensitive the surface energy is to the type of interaction potential assumed, in particular to find out whether a meson type interaction gave better agreement.*

§ 5. ON THE DEFINITION OF SURFACE ENERGY

We mentioned in the Introduction Feenberg's calculation of the surface energy. Feenberg found that for particles in a potential well of infinite depth the kinetic part of the surface energy was by itself about twice the total observed surface energy, but decreased when the well was made finite and could be made to account for about two-thirds of the total by choosing a depth of 28 Mev. The basis of Feenberg's calculations is the remark that the replacement of summation over states in momentum space by integration when evaluating the total kinetic energy of a system of particles in a potential well gives rise to a correction proportional to the two-thirds power of the number of particles and can therefore be thought of as a surface energy. On examination of Feenberg's method it became apparent that the interpretation of the $A^{2/3}$ term in the empirical binding energy formula as an energy associated with the surface region of a nucleus was justified only in certain circumstances and that the figure given by Feenberg for the kinetic part of the surface energy contains, as a consequence, an arbitrary part arising from an arbitrariness in the definition of surface energy which will be discussed below.

Broadly speaking this is due to the fact that if the total energy of a nucleus is considered as composed of a surface term associated with the surface region and a volume term associated with the rest of the nucleus it is generally assumed that

* Another factor which would tend to increase the ratio of surface to volume energy is a deviation of the nucleus from spherical shape. It can be shown, however, that for any reasonable deviation from spherical symmetry the effect on η is negligible. Thus if the nucleus were a prolate spheroid with the two axes in the ratio 0·8 the increase in η would be less than 1%, and even for a ratio 0·4 the increase would be only 13%.

the former is proportional to $A^{2/3}$ and the latter to A, although this is true only if the central or 'bulk' density of nuclear matter (the average density in a region excluding the surface) is independent of A. Otherwise the volume term may, in addition to the main term in A, contain a part proportional to $A^{2/3}$ which, as far as the empirical formula is concerned would be indistinguishable from the surface energy proper. Now, although the approximate independence of the bulk density on A is a well-established fact, small deviations from this law will be caused by the 'surface tension' itself as well as by the electrostatic repulsion between protons and possibly by other effects. For instance, the first of these causes can easily be shown to produce a deviation of the bulk density from a constant by an amount proportional to $A^{-1/3}$.* Hence the density of kinetic or potential energy in the bulk of the nucleus which is a function of the bulk density will also in general contain a variation proportional to $A^{-1/3}$ and its integral over the bulk of the nucleus will contain a term proportional to $A^{2/3}$ which will combine with the surface energy proper. On the other hand, the total volume energy (kinetic plus potential) is minimized with respect to the bulk density (at least in first approximation) and therefore the small change in bulk density will affect the total volume energy only in second order, giving a correction proportional to $A^{1/3}$. In the case of the change of density produced by the electrostatic forces the correction to the total energy is similarly of second order, although its dependence on A could in any case be used (at least in principle) to distinguish it from a surface term. Consequently when speaking of the *total* surface energy we can neglect to first order the small changes in the bulk density but when speaking of the surface energy as split into potential and kinetic contributions we must remember that each is composed of two parts of the same order of magnitude: (*a*) a surface energy proper (i.e. associated with the surface region) and (*b*) a term which is really part of the volume energy. We shall call the sum of (*a*) and (*b*) the 'apparent surface energy' (kinetic or potential). It is equal to what would appear as the second term in an analysis of the total kinetic or potential energy according to the formula $c_1A+c_2A^{2/3}$, c_1 and c_2 being constants. We see that proper and apparent surface energies would be equal only if the bulk density were kept constant,† except for the total surface energy which is independent of first order changes in density. As will be shown, the failure to recognize the fact that the definition of surface energy depends on what is assumed about the bulk density has led Feenberg to incorrect conclusions with regard to his calculations of surface energy.

The method employed by Feenberg of using exact summation in momentum space in place of integration to calculate the surface energy, together with the assumption that the size of the potential well is proportional to the number of particles can be shown to make the bulk density a definite function of A, the function being neither a constant nor the relation occurring in actual nuclei, and so the method imposes a certain quite arbitrary division of the total surface energy into apparent kinetic and potential parts. If the same model were used

* If the total energy of A particles in a well of volume V is written in the form

$$E=E_{\text{vol}}+E_{\text{surf}}=AF(\rho)+A^{2/3}G(\rho), \qquad \rho=A/V$$

then the condition $(\partial E/\partial V)_A=0$ gives $A^2F'(\rho)+A^{5/3}G'(\rho)=0$. For $A\to\infty$ this gives $F'(\rho_0)=0$ where ρ_0 is a constant. For A large but finite we then have, approximately: $A^{1/3}F'(\rho_0+\delta)+G'(\rho_0)=0$ so that $A^{1/3}F''(\rho_0)\delta+G'(\rho_0)=0$ and $\delta=\text{const.}\times A^{-1/3}$.

† More precisely if the bulk energy densities were kept constant. It can, however, be verified that the constancy of the particle density ensures the constancy of the energy densities to the required order of approximation.

consistently to calculate the potential surface energy as well, the total would still be correct. But Feenberg now makes use of the fact that because the potential surface energy is the result of the decreased binding of particles near the surface it must always be positive, and consequently the kinetic surface energy must be less in magnitude than the empirical total surface energy. This assumption is only valid for the proper potential surface energy and cannot be applied to the apparent energy which can be positive or negative depending on the assumed relation between the bulk density and A. In some of the cases considered by Feenberg (for example, a well of infinite depth) the implied relation between the bulk density and A is in fact such that the apparent kinetic surface energy is about five times the corresponding proper energy.

We have already shown how to calculate the proper surface energies by means of a semi-infinite distribution of particles, in which case summation in momentum space goes over to integration without approximation. (The surface energy given by a formula of the type $(4a)$ is associated with the surface region and is therefore a proper surface energy.) In what follows we shall show how Feenberg's procedure of retaining exact summation implies a certain relation between the bulk density and A and we shall verify that if from the apparent kinetic surface energy calculated in this way we subtract the part due to this variation of the bulk density the remainder agrees with the proper surface energy calculated by means of the semi-infinite model on the lines of §2.

For purposes of illustration we shall consider the case of A particles in a one-dimensional well of infinite depth and length L. In addition to a term proportional to L the total kinetic energy of such a system will contain a constant term which can be regarded as an 'end energy'. This end energy is in many ways analogous to the surface energy in the three-dimensional case and we shall use this fact to illustrate the foregoing discussion.

The wave functions of the particles in the well are $\sqrt{(2/L)}\sin(xp/\hbar)$, where x is measured from one end of the well. With one particle per state the density of states in momentum 'space' (a line extending from 0 to the maximum momentum P) is $2L/h$. Also $p=\pi\hbar k/L$, where $k=1, 2, 3, \ldots . A$. The total kinetic energy is then, without approximation:

$$T=\sum_p \frac{p^2}{2M}=(\pi^2\hbar^2/2ML^2)\sum_1^A k^2$$
$$=(\pi^2\hbar^2/6M)\{L(A/L)^3+(3/2)(A/L)^2+(2L)^{-1}(A/L)\}. \quad \ldots\ldots (11)$$

Feenberg's procedure is to assume the average density A/L constant. The first term in (11) is then a line energy (corresponding to a volume energy in a three-dimensional case), the second is a constant end energy $((\pi^2\hbar^2/8M)(A/L)$ per end) and the last vanishes for large L and will not be considered further. We note that the replacement of $\sum_1^A(\ldots.)$ by $(2L/h)\int_0^P(\ldots.)\,dp$ yields the first term only. An analogous calculation for a cubical or spherical well gives, in addition to the volume term, an energy proportional to $A^{2/3}$ which would not be present but for the use of an exact summation. These are the surface energies calculated by Feenberg. To show that they are not proper surface energies we shall calculate the bulk density and show that it is not constant if A/L is assumed constant. For this purpose consider the one-dimensional particle density as a function of x. Its general form near the ends of the well will be as shown in Figure 1, i.e. there will be a decrease of density near the ends in a region of the order of magnitude

of the wavelength of the most energetic particle. To make up for this the bulk density will be slightly greater than A/L; it is in fact given by $n_0=(A+\frac{1}{2})/L$.* The assumption $A/L=$ const. means therefore a bulk density differing from a constant by $(2L)^{-1}$. To see how much of the end energy calculated above is due to this variation, let us calculate the proper end energy by expanding (11) in powers of L^{-1} (or A) but keeping n_0 constant. This can be done conveniently by introducing the effective length of the particle distribution defined by $L'=A/n_0$. (It is the length which would contain A particles at a uniform density n_0.) Since $L=(1+1/2A)L'$ we can write (11) as

$$T=(\pi^2\hbar^2/6M)L'(A/L')^3+(\pi^2\hbar^2/12M)(A/L')^2+\text{lower powers of } A.$$

Since $A/L'=$ const., the proper end energy is given by the second term and is now $\Delta T=(\pi^2\hbar^2/24M)(A/L')^2$ per end, a third of the apparent energy.

For comparison let us calculate the proper end energy by using a semi-infinite distribution by means of the formula

$$\Delta T=t(\infty)\int_0^\infty \{t(x)/t(\infty)-n(x)/n(\infty)\}\,dx. \qquad \ldots\ldots(12)$$

Since summations are now replaced by integration the density $n(x)$ is

$$n(x)=(4/h)\int_0^P \sin^2(xp/\hbar)\,dp=n(\infty)\left(1-\frac{\sin X}{X}\right),$$

where $$n(\infty)=2P/h, \qquad X=2xP/\hbar.$$

Similarly $$t(x)=t(\infty)\left(1-\frac{3\sin X}{X}-\frac{6\cos X}{X^2}+\frac{6\sin X}{X^3}\right),$$

where $$t(\infty)=P^3/3hM.$$

Hence $\Delta T=P^2/24M=(\hbar^2\pi^2/24M)(A/L)^2$ which agrees with the value found above. (The difference between A/L and A/L' is immaterial since we require the end term to the lowest order in A.) Similar considerations apply in the three-dimensional case. For example, if in the case of an infinitely deep spherical well of volume V the bulk density is kept constant† the coefficient of the surface term is 0·194 times what it would be if A/V were constant. The proper surface energy obtained in this way agrees with the value corresponding to $x_l=\lambda_0/32$ obtained in § 2 by means of the semi-infinite model.

The conclusion of this section is that it is possible to calculate the proper surface energy without the use of exact summation in momentum space. This is important as otherwise the evaluation of the potential surface energy would be virtually impossible. Also the difficulties which Feenberg encountered in carrying out the summations for a spherical well in the case of 'incomplete shells' are absent and the generalization to wells of any shape presents no difficulties.

The conception of the semi-infinite distribution of particles which makes this possible is the natural model for calculations concerned with surface phenomena.

* The density as a function of x is

$$n(x)=(2/L)\sum_{k=1}^{A}\sin^2(k\pi x/L)=(A+\tfrac{1}{2})/L-\frac{\sin[\pi(2A+1)x/L]}{2L\sin(\pi x/L)}$$

exactly. The density rises gradually from zero at $x=0$, oscillates with decreasing amplitude about the value $(A+\frac{1}{2})/L$ and then goes to zero again at $x=L$.

† Only in the case of a cubical well can the bulk density be obtained easily by an explicit summation. A simple way of finding the bulk density for a well of any shape without the use of summations rests on the fact that the effective volume of a distribution of particles inside a well of volume V and surface S is $V-bS$, where b is an expression like (3). (If the sides of the well are not infinitely steep the limits of integration in (3) are from $-\infty$ to ∞.) The bulk density is then $n_0=A/(V-bS)$.

It is in a sense complementary to the conventional statistical model of the nucleus. For instance, just as it is the aim of the latter to derive theoretically the volume term in the binding energy formula, so it is the aim of the former to calculate the surface term. We saw how through the inter-dependence of the two parallel calculations some of the uncertainties of the statistical treatment can be avoided.

§6. DERIVATION OF CERTAIN FORMULAE

Equations (8) to (10) are obtained as follows: the momentum of a particle at x is $p=\sqrt{(p_x^2+p_y^2+p_z^2)}=\sqrt{(p_x^2+p_\perp^2)}$, where

$$p_x=\begin{cases}\text{const.}=p_\infty^2 & \text{for } x>0\\ p_\infty^2-2MV(x) & \text{for } x<0\end{cases}$$

in the notation of §2. Hence

$$n(x)=\sum_{\mathbf{p}}\psi_{\mathbf{p}}^*\psi_{\mathbf{p}}=(8/h^3)\int_{p_\infty=0}^{P}dp_\infty\int_{p_\perp=0}^{\sqrt{(P^2-p_\infty^2)}}q^2 2\pi p_\perp\,dp_\perp$$

$$=(8\pi P^3/h^3)\int_{p_\infty=0}^{P}\{1-(p_\infty/P)^2\}q^2\,d(p_\infty/P)\quad\text{(neutrons only).}$$

Therefore

$$n(x)/n(\infty)=3\int_0^1(1-S^2)q^2\,dS\quad\text{(neutrons or neutrons and protons).}$$

Since $p_\infty/P=\theta/\theta_0=S$, q in the above stands for $q(\theta_0 S,\chi)$. This proves (8). To find $t(x)$ we calculate

$$t(x)=(8/2Mh^3)\int_{p_\infty=0}^{P}dp_\infty\int_{p_\perp=0}^{\sqrt{(P^2-p_\infty^2)}}(p_\infty^2-2MV(x)+p_\perp^2)q^2 2\pi p_\perp\,dp_\perp.$$

Integration over $p_\perp$ gives (9). To prove (10) we calculate the mixed density first:

$$n(\mathbf{r},\mathbf{r}')=\sum_{\mathbf{p}}\psi_{\mathbf{p}}^*(\mathbf{r})\psi_{\mathbf{p}}(\mathbf{r}')$$

$$=(8/h^3)\iiint\exp\{i\mathbf{p}_\perp\cdot(\mathbf{r}_\perp'-\mathbf{r}_\perp)/\hbar\}\cdot qq',$$

where $\mathbf{p}_\perp$ and $\mathbf{r}_\perp$ are the two-dimensional vectors (p_y, p_z) and (y, z) respectively, and q' stands for q at the point x'.

Putting $r_\perp=0$ and denoting by Θ the angle between $\mathbf{p}_\perp$ and $\mathbf{r}_\perp'$ we have

$$n(\mathbf{r},\mathbf{r}')=(16/h^3)\int_{p_\perp=0}^{P}dp_\perp p_\perp\int_0^\pi d\Theta\exp(ip_\perp r'_\perp\cos\Theta/\hbar)\cdot F(p_\perp,x,x'),$$

where

$$F(p_\perp,x,x')=\int_{p_x=0}^{\sqrt{(P^2-p_\perp^2)}}qq'\,dp_x.$$

For a gaussian interaction $v(x)$ is then given by

$$\text{const.}\iiint_{x',y',z'=-\infty}^{\infty}\exp\{-[(x'-x)^2+y'^2+z'^2]/a^2\}\,|n(\mathbf{r},\mathbf{r}')|^2\,dx'\,dy'\,dz'$$

$$=\text{const.}\int_{x'=-\infty}^{\infty}dx'\exp[-(x'-x)^2/a^2]\int_{p_\perp=0}^{P}\int_{p_\perp'=0}^{P}\int_{\Theta=0}^{\pi}\int_{\Theta'=0}^{\pi}dp_\perp\,dp_\perp'\,d\Theta\,d\Theta'FF'$$

$$\times\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dy'\,dz'\exp\{-(y'^2+z'^2)/a^2+i[y'(p_y-p_y')+z'(p_z-p_z')]/\hbar\},\qquad\ldots\ldots(13)$$

where F' stands for $F(p_\perp',x,x')$.

The y' and z' integrations give

$$a^2\pi \exp\{-a^2[(p_y-p_y')^2+(p_z-p_z')^2]/4\hbar^2\}$$
$$= a^2\pi \exp\{-a^2(p_\perp^2+p_\perp'^2)/4\hbar^2+(a^2p_\perp p_\perp' \cos\phi)/2\hbar^2\},$$

where ϕ = angle between $\mathbf{p}_\perp$ and $\mathbf{p}_\perp' = \Theta' - \Theta$. Hence one of the Θ integrations gives simply π and therefore

$$v(x) = \text{const.} \int_{x'=-\infty}^{\infty} dx' \exp[-(x'-x)^2/a^2] \int_{p_\perp=0}^{P}\int_{p_\perp'=0}^{P} dp_\perp\, dp_\perp' p_\perp p_\perp' FF'$$
$$\times \exp[-a^2(p_\perp^2+p_\perp'^2)/4\hbar^2] \int_{\varphi=0}^{\pi} d\phi \exp[(ap_\perp p_\perp' \cos\phi)/2\hbar^2].$$

The last integral is $\pi \sum_{m=0}^{\infty} (a^2p_\perp p_\perp'/4\hbar^2)^{2m}/(m!)^2$ and so the double integration over $p_\perp$, $p_\perp'$ can be written as a sum of squares of single integrals:

$$v(x) = \text{const.} \int_{-\infty}^{\infty} dx' \exp[-(x'-x)^2/a^2]$$
$$\times \sum_{m=0}^{\infty} \left\{\frac{1}{m!} \int_{p_\perp=0}^{P} dp_\perp p_\perp^{2m+1} (a/2\hbar)^{2m} F \exp[-a^2p_\perp^2/4\hbar^2]\right\}^2.$$

Using the definition of F and re-arranging the terms in the curly brackets we obtain equation (10). The multiplying constant can be checked by taking the limit $x \to \infty$ when $v(x)/v(\infty)$ should reduce to unity. In practice only the first three or four terms of the sum are required. Even so, to obtain x_v, a triple numerical integration is necessary, starting with the function $q(\theta_0 S, \chi)q(\theta_0 S, \chi')$ of three variables. The work was made particularly difficult by the oscillatory nature of q. For example, to calculate x_v for a single choice of the parameters a and x_0 requires some 600 numerical integrations. Special techniques (usually combinations of the Gregory and central difference formulae) were used to obtain maximum efficiency with a minimum of entries. ζ_v was calculated for $\omega_0 = 1{\cdot}00$ and $\theta_0 = 0$, $0{\cdot}7$, $1{\cdot}0$ which corresponds to the circled points in Figure 2.

§7. SPECIAL CASES

Some limiting cases can be evaluated more simply:

(i) For small ζ_0 we find $\zeta_v(\zeta_0) = 0{\cdot}1963 - 0{\cdot}3050\zeta_0^{1/3} + \ldots$.

(ii) For $\zeta_0 = 0$ and $a \ll \lambda_0/2\pi(\omega_0 \ll 1)$ we find $\zeta_v = (3\pi/40)\{1 - (13/35)\omega_0^2 + \ldots\}$.

When $a \to 0$ the interaction becomes a δ-function but ζ_v tends to the finite limit $0{\cdot}2356$ which is, in fact, not very different from the case $\omega_0 = 1$ ($\zeta_v = 0{\cdot}174$). In this limit the following very simple formula holds for any density distribution:

$$x_v = \int_{-\infty}^{\infty} [n(x)/n(\infty) - \{n(x)/n(\infty)\}^2]\, dx.$$

(iii) $\zeta_0 \gg 1$. This case has been treated by Bethe and Bacher (1936, §29). The gradient of the potential $V(x)$ in the surface being small we can use the conventional Thomas–Fermi formula for t and the corresponding expression for v as given by (7) to obtain these quantities as functions of n. For a linear $V(x)$, n itself is proportional to the 3/2 power of the distance across the surface and therefore $t(x)$ and $v(x)$ can be found.

Explicitly, if y is the distance measured from $x=-x_0$ as origin, then in the region $0 \leqslant y \leqslant x_0$ we have

$$n(x)/n(\infty)=(y/x_0)^{3/2}, \qquad t(x)/t(\infty)=(y/x_0)^{5/2},$$
$$v(x)/v(\infty)=\omega^3 f(2\omega)/\omega_0{}^3 f(2\omega_0)$$

where $\omega/\omega_0=(y/x_0)^{1/2}$ and $n(\infty)$, $t(\infty)$, $v(\infty)$ are the values of n, t, v for $y \geqslant x_0$.

It follows elementarily that,

$$\zeta_t=-(4/35)\zeta_0=-0{\cdot}1143\zeta_0,$$
$$\zeta_v=(3/5)\{(2\omega_0)^2/2-2+3/(2\omega_0)^2-[1+3/(2\omega_0)^2]\exp[-(2\omega_0)^2]\}\zeta_0/(2\omega_0)^3 f(2\omega_0)$$
$$=0{\cdot}1038\zeta_0 \qquad \text{for } \omega_0=1.$$

These are the asymptotes shown in Figure 2.

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Directional Correlation Between Successive Internal-Conversion Electrons: II*

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ABSTRACT. A previous paper examined the directional correlation $I(\theta)$ between two conversion electrons in cascade, each electron being ejected, with energy much less than mc^2, from an initial s-state, under the action of a pure electric multipole γ-transition, and $I(\theta)$ was shown to be completely determined by symmetry arguments alone in this case. In the present paper we consider the same problem for pure magnetic, and for mixed transitions. Here $I(\theta)$ usually appears as a weighted mixture of constituents $I_1(\theta)$, $I_2(\theta)$, etc., each of which is completely determined by symmetry arguments alone. The weight factors, however, must be determined from standard internal-conversion theory.

§ 1. INTRODUCTION

We consider an atom in which two nuclear transitions in cascade, $A \rightarrow B \rightarrow C$, are accompanied by the emission from the atom of two successive internal-conversion electrons. In a previous paper (Gardner 1949, this paper will be referred to as I) it was pointed out that from general considerations of angular momentum conservation one would expect the emission

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directions of the two electrons to be correlated, and that this correlation should depend on the angular momenta of the nuclear levels A, B, C and the ejected electrons.

Paper I is limited to electric internal conversion, that is to say it is applicable to transitions in which a magnetic multipole is absolutely forbidden by the selection rules, and to mixed transitions in which the number of conversion electrons associated with the magnetic multipole is negligible compared with the number associated with the electric. There are, however, transitions, not uncommon, in which magnetic conversion cannot be neglected, and may indeed far exceed electric conversion (cf. Drell 1949 *); and, less commonly, there are transitions in which an electric multipole is absolutely forbidden by the selection rules. It is the purpose of the present paper to extend the earlier calculations to cases in which either or both transitions in the cascade $A \rightarrow B \rightarrow C$ are pure magnetic multipole in character. The results of such calculations, together with those of I, will enable one also to predict the directional correlation when either or both of the cascade transitions give rise to a mixture of electric and magnetic conversion. This is because in angular correlations involving conversion electrons (c–c or γ–c) there are no interference effects as in γ–γ correlation, and therefore the relative angular distribution of successive electrons from a mixed cascade is simply a weighted mixture of the distributions given by the appropriate pure cascades, the weight factor depending on the relative intensities of the electric and magnetic multipoles and on the conversion coefficients.†

Apart from those relating to the character of the transitions, the initial postulates of I apply unmodified in the present paper. Recapitulating, they are: (*a*) the life-time of the nuclear state B is small compared with the precession period of the nucleus in whatever external fields may be present; (*b*) the total angular momentum of all the orbital electrons, other than the ejected ones, remains constant throughout; (*c*) each ejected electron comes from an initial s-state (but not necessarily the K-shell); (*d*) the kinetic energy, after ejection, of each conversion electron is very much less than its rest-energy mc^2.

General expressions for the angular correlation function $I(\theta)$ are derived for the cases magnetic–electric cascade (or electric–magnetic cascade), and magnetic–magnetic cascade. For each of these cases $I(\theta)$ appears as a weighted mixture of two or more constituent distributions $I_1(\theta)$, $I_2(\theta)$ etc. These constituent distributions are always, in principle, completely determined by symmetry arguments alone and can be manipulated into a form (usually an expansion linear in Legendre polynomials $P_k(\cos\theta)$, with $k=0, 2, 4\ldots.$) fairly convenient for practical computation, at any rate for low values of the angular momenta of the nuclear levels and the ejected electrons. The weight factors involve essentially the matrix elements for the various possible electron transitions; these matrix elements can be calculated from standard internal-conversion theory: numerical values for certain cases have been published by Berestetzky (1948 a). Even

* A more recent paper by Axel and Dancoff (1949) quotes calculations by Rose and collaborators which show magnetic conversion to be even greater—sometimes by a factor of 3—than Drell estimated.

† The absence of interference in c–c correlations was noticed by the present author in the course of this work. Fierz (1949) has shown that so long as at least one of the particles is a conversion electron there is no interference, whether the other particle be an electron or a γ-quantum. It should be mentioned, however, that these results were derived on the assumption that each conversion electron comes from an initial s-state; when this assumption is removed interference effects would appear to be possible (cf. Ling and Falkoff 1949), but we shall not be concerned with such cases in the present paper.

without a knowledge of the weight factors it is possible to infer certain general properties of $I(\theta)$ from the form of $I_1(\theta)$, $I_2(\theta)$ etc. Occasionally it can be seen from the angular momentum relations that all weight factors except one must vanish, * in which case $I(\theta)$ reduces to the appropriate constituent distribution.

The general theory of angular correlation in successive γ-transitions, with or without internal conversion, has been presented, independently, by Berestetzky (1948 b) and by Fierz (1949). Owing to their generality, however, the results of these papers are not readily applicable to practical cases. The treatment of the present paper, and of I, while restricted to c–c correlation, has the advantage of leading fairly directly to formulae suitable for practical computation, at any rate when at least one of the transitions is electric multipole; for the magnetic–magnetic cascade there is, perhaps, little to choose between the two treatments.

§ 2. SUCCESSIVE PURE TRANSITIONS OF DIFFERENT CHARACTER

In this section we shall assume that in the cascade $A \rightarrow B \rightarrow C$ one of the transitions is pure electric, and the other pure magnetic. For the sake of definiteness we take the first transition to be magnetic 2^{L_1}-pole and the second to be electric 2^{L_2}-pole; it will be clear from physical considerations, however, that the cascades, A (magnetic 2^{L_1}-pole) B (electric 2^{L_2}-pole) C and C (electric 2^{L_2}-pole) B (magnetic 2^{L_1}-pole) A, must give the same angular correlation. After deriving a general formula for $I(\theta)$ and discussing qualitatively its properties, we consider its transformation into a form more suitable for practical interpretation and computation, namely an expansion linear in the even order spherical harmonics, $Y_{k0}(\theta, 0)$, or, what is effectively the same thing, Legendre polynomials $P_k(\cos\theta)$.

(i) *Derivation and Properties of General Formula*

Keeping to the nomenclature of I we denote the angular momenta of the nuclear levels A, B, C, by $\mathbf{J}_A$, $\mathbf{J}_B$, $\mathbf{J}_C$, and the orbital angular momenta of the electrons, after ejection, by $\mathbf{l}_1$, $\mathbf{l}_2$. The projections of these quantum-vectors on the (arbitrary) z-axis we denote by M_A, M_B, M_C, m_1, m_2. It is also necessary to introduce quantum-vectors $\mathbf{s}'$, $\mathbf{s}$ (z-components $m_{s'}$, m_s) representing the spin of the first electron before and after conversion respectively: we must do this because magnetic multipole conversion, even at low energies, involves the spin interaction—in fact magnetic conversion in the K-shell is entirely a spin effect (see, for example, Berestetzky 1946). Two further quantities will be required, namely $\mathbf{J}_A'$, $\mathbf{j}$ (z-components M_A', m_j) defined by:

$$\mathbf{J}_A' \equiv \mathbf{J}_A + \mathbf{s}', \qquad \ldots\ldots(1)$$

$$\mathbf{j} \equiv \mathbf{l}_1 + \mathbf{s}, \qquad \ldots\ldots(2)$$

$$M_A' \equiv M_A + m_{s'}, \qquad \ldots\ldots(3)$$

$$m_j \equiv m_1 + m_s. \qquad \ldots\ldots(4)$$

Thus $\mathbf{J}_A'$ is the total angular momentum of the whole system, nucleus plus two electrons, † and $\mathbf{j}$ the total angular momentum of the first electron after ejection. In general J_A' can have either of the values $J_A \pm \frac{1}{2}$, and j either of the values

* Or that $I_1(\theta) = I_2(\theta)$, etc.

† We may ignore the spin of the second electron, since to a non-relativistic approximation electric multipole conversion does not involve spin interaction (cf. § 4, and I).

$l_1 \pm \frac{1}{2}$. However, the main argument may be carried through as if J_A', j each had one definite value, and a summation (with appropriate weight factors) over J_A', j introduced at the end.

Simple considerations of parity and angular momentum conservation give the following relations between the multipole orders L_1, L_2 and the electron angular momenta (cf. Berestetzky 1946):

$$l_1 = L_1 + 1 \quad (\text{for } j = l_1 - \tfrac{1}{2}), \qquad \ldots\ldots(5)$$

$$l_1 = L_1 - 1 \quad (\text{for } j = l_1 + \tfrac{1}{2}), \qquad \ldots\ldots(6)$$

$$l_2 = L_2. \qquad \ldots\ldots(7)$$

Also the principle of angular momentum conservation gives, applied to the A→B transition:

$$\mathbf{J}_A' = \mathbf{J}_B + \mathbf{j}, \qquad \ldots\ldots(8)$$

$$M_A' = M_B + m_j \qquad \ldots\ldots(9)$$

and applied to the B→C transition:

$$\mathbf{J}_B = \mathbf{J}_C + \mathbf{l}_2 \qquad \ldots\ldots(10)$$

$$M_B = M_C + m_2. \qquad \ldots\ldots(11)$$

Since $\mathbf{J}_A'$ is constant throughout we write $\psi(J_A', M_A')$ for the wave function of the whole system in the final state. Similarly, following the procedure of I, we introduce the final-state wave functions: $\psi_B(J_B, M_B)$, $\psi_C(J_C, M_C)$, $\phi(j, m_j)$, $\psi_1(l_1, m_1)$, $\psi_2(l_2, m_2)$, $\chi(s, m_s)$ for the systems characterized by the quantum numbers in brackets in each case. Where no ambiguity occurs $\psi_A(J_A', M_A')$ will be written simply as ψ_A, with similar abbreviations for the other wave functions.

We now use the standard results for the vector addition of commuting angular momenta (see, for example, Condon and Shortley 1935) to obtain ψ_A as a suitable combination of the other wave functions. Thus, in view of (2) we can express each $\phi(j, m_j)$ as a linear combination of the $2l_1 + 1$ possible $\psi_1(l_1, m_1)$ corresponding to a definite l_1, and the two possible spin functions $\chi(s, \frac{1}{2})$, $\chi(s, -\frac{1}{2})$:

$$\phi \sim \sum_{m_1, m_s} C^{jm_j}_{l_1 m_1 s m_s} \psi_1 \chi. \qquad \ldots\ldots(12)$$

Similarly, through (8), ψ_A is obtained as a linear combination of the ψ_B and ϕ, and, through (10), ψ_B as a linear combination of the ψ_C and ψ_2. Hence, combining results:

$$\psi_A \sim \sum_{\substack{M_B, m_j, M_C \\ m_2, m_1, m_s}} C^{J_A' M_A'}_{J_B M_B j m_j} C^{J_B M_B}_{J_C M_C l_2 m_2} C^{jm_j}_{l_1 m_1 s m_s} \psi_C \psi_1 \psi_2 \chi. \qquad \ldots\ldots(13)$$

The C's in (12) and (13) are the coefficients common to all problems in which two angular momenta are combined to give a resultant. References dealing with their derivation and properties are given in I.

The angular parts of ψ_1, ψ_2 are the spherical harmonics $Y_{l_1, m_1}(\theta_2, \phi_1)$, $Y_{l_2, m_2}(\theta_2, \phi_2)$. If we now define the (hitherto arbitrary) z-axis as the emission direction of the first electron by setting $\theta_1 = \phi_1 = 0$ the angular correlation function will be $I(\theta_2, \phi_2)$, involving only the coordinates θ_2, ϕ_2 of the second electron. Another simplification resulting from this choice of z-axis is that zero is the only admissible value of m_1, so that $m_s = m_j$ (cf. I). $I(\theta_2, \phi_2)$ is obtained from (13) by

$$I(\theta_2\, \phi_2) \sim \sum_{M_A'} \int \psi_A^* \psi_A d\tau \qquad \ldots\ldots(14)$$

where the integration is over all coordinates except θ_2, ϕ_2 and where the summation over M_A' has to be introduced because $\psi_A(J_A', M_A')$ refers to a definite M_A', whereas experimentally it is the average over all the $2J_A'+1$ possible values of M_A' that is observed. The integrand in (14) is a product of two sums; when this is multiplied out and integrated it is found that the orthogonality properties of the ψ_C and the χ_1 eliminate the cross terms, leaving only square terms. We have then omitting such constant factors as $|\psi_C|^2, |Y_{l_1,0}(0,0)|^2$, and noting that $|Y_{l_2,m_2}(\theta_2,\phi_2)|^2$ is independent of ϕ_2:

$$I(\theta_2) \sim \sum_{\substack{M_A', M_B, m_s, \\ M_C, m_2}} |C^{J_A' M_A'}_{J_B M_B j m_s} C^{J_B M_B}_{J_C M_C l_2 m_2} C^{j m_s}_{l_1 0 m_s} \chi Y_{l_2,m_2}(\theta_2, 0)|^2. \quad \ldots\ldots(15)$$

In (15), $|\chi(s, m_s)|^2$ may be omitted as a factor common to every term provided the values $\pm\frac{1}{2}$ for m_s are equally likely. This is certainly true in the absence of a magnetic field. In a field H it is still approximately true provided the magnetic interaction energy μH of the electron is only a small perturbation to its total energy. A simple calculation shows that it is only for fields greater than 10^9 gauss that μH becomes appreciable, so for all practical purposes we may omit $|\chi|^2$ from (15) as a common factor.

For the summation over m_s the factor $|C^{j m_s}_{l_1 0 m_s}|^2$ is also constant, since by a general property of the C's it is the same whether $m_s = \pm\frac{1}{2}$. It is, however, different for $j = l_1 + \frac{1}{2}$ and $j = l_1 - \frac{1}{2}$ and must therefore be included in the weight factor when writing out expressly the terms for these two different values of j. Recalling also that the final expression for the angular correlation function must include a sum over J_A' as well as j, we have from (15) (replacing θ_2 by θ since the suffix can now be dropped without ambiguity):

$$I(\theta) = \sum_{J_A', j} \sum_{\substack{M_A', M_B, m_s \\ M_C, m_2}} G_j |C^{J_A' M_A'}_{J_B M_B j m_s} C^{J_B M_B}_{J_C M_C l_2 m_2} Y_{l_2,m_2}(\theta, 0)|^2. \quad \ldots\ldots(16)$$

Here G_j is a weight factor which depends on the matrix elements for the electron transitions to the two possible final states $j = l_1 \pm \frac{1}{2}$, and also includes the factor $|C^{j 0}_{l_1 0 s}|^2$. The relative weighting for the two values of J_A' is automatically taken care of by the summation over the magnetic sub-states M_A'.

Formula (16) represents an angular distribution symmetrical about the z-axis and the equatorial plane. Obviously by an alternative choice of z-axis $I(\theta)$ could be expressed in terms of $|Y_{l_1,m_1}(\theta,0)|^2$ instead of $|Y_{l_2,m_2}(\theta,0)|^2$. This means that the highest power of $\cos^2\theta$ in (16) cannot exceed l_1 or l_2, whichever is lower; or in terms of multipole orders the highest power of $\cos^2\theta$ cannot exceed the order of the electric multipole transition or one plus the order of the magnetic multipole transition, whichever is lower. When $J_A = J_C = 0$, (16) reduces to a particularly simple form, namely $I(\theta) \sim |Y_{J_B,0}(\theta,0)|^2$ (as does (10) of I). A few other simple cases, where all the angular momenta have small values (including zero), may be calculated from (16) without difficulty. However, for numerical calculations with higher angular momenta the formula as it stands is impracticable owing to the labour involved in the summations. It is also necessary in general to know the ratio of the weight factors G_j for summing over the two values of j*.

* In the example $J_A = J_C = 0$ it is not, however, necessary to know $G_{L_1+\frac{1}{2}}/G_{L_1-\frac{1}{2}}$. This is because the constituent angular distributions corresponding to $j = L_1 + \frac{1}{2}$ and $j = L_1 - \frac{1}{2}$ both behave as $|Y_{J_B,0}(\theta,0)|^2$ so that any weighted mixture of them must do the same.

(ii) *Expansion into $Y_{k,0}$: Discussion*

The right-hand side of (16) can be manipulated into a form more convenient for practical calculation and interpretation by replacing $|Y_{l_\nu, m_\nu}(\theta,0)|^2$ by its expansion in terms of $Y_{k,0}(\theta,0)(k=0,2,4\ldots)$ and then using the results of Racah (1942) to evaluate the coefficients of the $Y_{k,0}(\theta,0)$ in the resulting formula. The details of this method are explained in I, where the coefficients of $Y_{k,0}(\theta,0)$ are expressed in terms of the Racah W functions. There is however one complication in the present case, which was absent in I, and this is concerned with the summation over M_A'(which is equal to $M_A \pm \frac{1}{2}$, by (3)). When $J_A' = J_A - \frac{1}{2}$, M_A' can assume any of the $2J_A'+1$ values $-J_A', -J_A'+1, \ldots J_A'$, and the result of the summation is given by a direct substitution in the appropriate formula of Racah. However, when $J_A' = J_A + \frac{1}{2}$, M_A' can go only from $-J_A'+1$ to J_A' ($M_A' = M_A + \frac{1}{2}$), or from $-J_A'$ to $J_A'-1$ ($M_A' = M_A - \frac{1}{2}$). In these cases therefore it is necessary to subtract one term from the result given by Racah's formula. Actually it is found that this correction term is zero unless J_B exceeds J_A and is integral*. For comparison with the results of I we write the final expression for $I(\theta)$ in terms of $P_k(\cos\theta)$ instead of $Y_{k,0}(\theta,0)$ where $P_k(\cos\theta)$ is the normalized Legendre polynomial related to $Y_{k,0}(\theta,0)$ in the familiar way (cf. I). We have then, finally,

$$I(\theta) \sim \sum_k B_k P_k(\cos\theta) \qquad \ldots\ldots(17)$$

with
$$B_k = (2k+1)^{-1/2}\, C^{k0}_{l_\nu 0 l_\nu 0}\, W(J_B J_C k l_2; l_\nu J_B) \times \sum_{j=L_1-\frac{1}{2}}^{L_1+\frac{1}{2}} G_j \{ J_A C^{k0}_{j\frac{1}{2}j-\frac{1}{2}}\, W(J_B \overline{J_A - \tfrac{1}{2}} k j; j J_B) + (J_A+1) C^{k0}_{j\frac{1}{2}j-\frac{1}{2}} W(J_B \overline{J_A + \tfrac{1}{2}} k j; j J_B) - T_k(J_A, J_B, j)\} \qquad \ldots\ldots(18)$$

Here $T_k(J_A, J_B, j)$ is the correction term arising from the summation over M_A'; it is given by,

$$T_k(J_A, J_B, j) = \tfrac{1}{2}(2k+1)^{1/2}\, C^{J_B, J_A+1}_{J_B, J_A+1;\, k, 0} \{ C^{J_A+\frac{1}{2}, J_A+\frac{1}{2}}_{J_B, J_A+1; j, -\frac{1}{2}} \}^2 \qquad \ldots\ldots(19)$$

when J_B is integral and is greater than or equal to J_A+1, and vanishes otherwise.

The ratio of the weight factors $G_{L_1+\frac{1}{2}}$ and $G_{L_1-\frac{1}{2}}$ involves the ratio of the matrix elements for the $j = L_1 + \frac{1}{2}$ and $j = L_1 - \frac{1}{2}$ transitions. If these matrix elements are calculated on the basis of the Pauli two-component theory of the spinning electron it appears that the $j = L_1 - \frac{1}{2}$ term is negligible so long as the atomic number Z is not too high (say <40). Such calculations have been made by Goertzel and Lowen (1945) and, independently, by Berestetzky (1946). However, Drell (1949) has shown that, even when the electron energy is very much less than mc^2, the Pauli theory is not valid for magnetic internal conversion, owing to the extremely singular nature of the magnetic multipole potential. Dirac theory must therefore be used in computing the matrix elements†; they will depend on Z, on the multipole order L_1 of the transition, and on the energy $h\nu$ associated with it. Their ratio will not in general vanish, but may occasionally do so in simple cases.

In practical applications the ratio $G_{L_1+\frac{1}{2}}/G_{L_1-\frac{1}{2}}$ would have to be evaluated numerically for the Z, L_1 and $h\nu$ applicable to the case in hand.‡ The labour of this

* If J_B is integral it follows from the angular momentum relations that J_A and J_C are also integral.

† It is only in describing the interaction of the electrons with the magnetic multipole field that the Pauli theory breaks down; it is quite adequate for describing the low-energy electrons in the continuum state after ejection, as was implied by our earlier use of the two-valued spin function χ.

‡ Berestetzky in a later paper (1948 a) tabulates numerical values of the matrix elements occurring in $G_{L_1+\frac{1}{2}}$ and $G_{L_1-\frac{1}{2}}$; the tables include values of L_1 from 1 to 5 and of $(h\nu/mc^2)(137^2/Z^2)$ from 0·625 to 10. In this second paper Berestetzky treats magnetic conversion by Dirac theory, and obtains results in agreement with Drell's.

operation is the same whether we use expression (16) or (17) for $I(\theta)$, but in other respects (17) has the advantage over (16), in that laborious summations over magnetic quantum numbers have been eliminated. The C's and W's in (18) can be found in tables*, or if these are not readily available, they may be calculated fairly quickly from general formulae (given, for example, in Racah's paper) which simplify considerably for values of the parameters likely to occur in practical cases.

It is interesting to compare the B_k of (17) (magnetic–electric cascade) with the corresponding coefficients in (18) of I (electric–electric cascade). These latter may be written

$$B_k' = C^{k0}_{l_1 0 l_1 0}\, W(J_B J_C k l_2;\, l_2 J_B)\; C^{k0}_{l_2 0 l_1 0}\, W(J_B J_A k l_1;\, l_1 J_B). \quad \ldots\ldots (20)$$

On comparing (18) and (20) we see that the part of B_k due to the electric transition, viz. $C^{k0}_{l_1 0 l_1 0}\, W(J_B J_C k l_2;\, l_2 J_B)$, remains unchanged; the factor $C^{k0}_{l_1 0 l_1 0}\, W(J_B J_A k l_1;\, l_1 J_B)$ is replaced in (18) by a considerably more complicated factor due to the magnetic transition. This comparison emphasizes the simplification obtained by the neglect of spin interaction, which, we saw, is permissible for electric multipole transitions but not magnetic. It is worth noting that the appearance of $W(J_B J_C k l_2;\, l_2 J_B)$ in B_k limits the complexity of $I(\theta)$ in (17), just as it does in (18) of I, for this W function vanishes unless $k \leqslant 2J_B$. In particular $J_B = 0$ or $\frac{1}{2}$ means that $I(\theta)$ is isotropic. This is another useful result arising from the expansion into $P_k(\cos\theta)$, for, although it might have seemed plausible from physical considerations, it is not readily proved from (16).

In I it was clear that the formula for $I(\theta)$ was unaffected by 'inverting' the cascade (i.e. interchanging J_A with J_C and l_1 with l_2). In the present case our formula (18) does not readily lend itself to investigating analytically the effect of inverting the cascade.† However, physical considerations tell us that J_A(magnetic 2^{L_1}–pole) J_B (electric 2^{L_2}–pole) J_C and J_C (electric 2^{L_2}–pole) J_B (magnetic 2^{L_1}–pole) J_A must give the same $I(\theta)$. This is immediately clear if one recalls that the interaction operators must be Hermitian, so that the total transition probability for the whole cascade is unaffected by a symmetrical interchange of angular momenta.

§3. SUCCESSIVE PURE MAGNETIC TRANSITIONS

(i) *Derivation of General Correlation Formula*

In this section we shall assume both transitions in the cascade $A \rightarrow B \rightarrow C$ to be pure magnetic multipole, of order L_1 and L_2 respectively. As before, we introduce the vectors $\mathbf{J}_A$, $\mathbf{J}_B$, $\mathbf{J}_C$, $\mathbf{l}_1$, $\mathbf{l}_2$, and their z-components M_A, M_B, M_C, m_{l_1}, m_{l_2}‡. For the spin vectors of the first electron before and after ejection we write $\mathbf{s}_1'$, $\mathbf{s}_1$ with z-components $m_{s_1'}$, m_{s_1}; for the second electron we have the corresponding

* Tables of C's are given, for example, by Condon and Shortley (1935, pp. 76–77); tables of W's have been prepared by Professor Jahn of Southampton for publication in due course.

† If one wanted to investigate this analytically, it were better to revert to (16) and apply an argument which Spiers has used (1948) in developing symmetry methods for discussing directional effects in general radioactive processes. This argument confirms the physically obvious result that inversion of the cascade leaves $I(\theta)$ unaffected.

‡ m_{l_1}, m_{l_2} are the quantities hitherto written m_1, m_2; the **J**'s, **l**'s and M's remain as defined at the beginning of § 2 (i).

quantities $\mathbf{s}_2'$, $\mathbf{s}_2$, $m_{s_2'}$, m_{s_2}. It is also convenient to define vectors $\mathbf{J}_A'$, $\mathbf{J}_B'$, $\mathbf{j}_1$, $\mathbf{j}_2$, with z-components M_A', M_B', m_{j_1}, m_{j_2}, by the relations:

$$\mathbf{J}_A' \equiv \mathbf{J}_A + \mathbf{s}_1' + \mathbf{s}_2' \quad \ldots\ldots(21) \qquad M_A' \equiv M_A + m_{s_1'} + m_{s_2'} \quad \ldots\ldots(25)$$

$$\mathbf{J}_B' \equiv \mathbf{J}_B + \mathbf{s}_2' \quad \ldots\ldots(22) \qquad M_B' \equiv M_B + m_{s_2'} \quad \ldots\ldots(26)$$

$$\mathbf{j}_1 \equiv \mathbf{l}_1 + \mathbf{s}_1 \quad \ldots\ldots(23) \qquad m_{j_1} \equiv m_{l_1} + m_{s_1} \quad \ldots\ldots(27)$$

$$\mathbf{j}_2 \equiv \mathbf{l}_2 + \mathbf{s}_2 \quad \ldots\ldots(24) \qquad m_{j_2} \equiv m_{l_2} + m_{s_2} \quad \ldots\ldots(28)$$

Thus $\mathbf{J}_A'$ is the total angular momentum of the whole system, nucleus plus two electrons, and remains constant throughout; $\mathbf{J}_B'$ is the total angular momentum of the system, nucleus plus second electron, in the intermediate and final states; $\mathbf{j}_1$, $\mathbf{j}_2$ are respectively the total angular momenta of the first and second electrons after ejection. In general $\mathbf{J}_A'$ can have any of the values $J_A, J_A \pm 1$; J_B' the values $J_B \pm \frac{1}{2}$; j_1 the values $l_1 \pm \frac{1}{2}$; and j_2 the values $l_2 \pm \frac{1}{2}$. However, the main part of the argument leading to $I(\theta)$ can be carried through as if J_A', J_B', j_1, j_2 each had one definite value; a weighted summation over the various alternative values is then carried out at the end, as was done in § 2.

The relations between the orbital angular momenta of the ejected electrons and the multipole orders of the transitions are (cf. equations (5) to (7)):

$$l_1 = L_1 + 1 \ \text{(for } j_1 = l_1 - \tfrac{1}{2}) \quad \ldots\ldots(29)$$

$$l_1 = L_1 - 1 \ \text{(for } j_1 = l_1 + \tfrac{1}{2}) \quad \ldots\ldots(30)$$

$$l_2 = L_2 + 1 \ \text{(for } j_2 = l_2 - \tfrac{1}{2}) \quad \ldots\ldots(31)$$

$$l_2 = L_2 - 1 \ \text{(for } j_2 = l_2 + \tfrac{1}{2}) \quad \ldots\ldots(32)$$

As before, we must introduce final-state wave functions for the systems characterized by the various quantum numbers. Thus for the whole system, nucleus plus two electrons, characterized by J_A', M_A', we write ψ_A (J_A', M_A') or briefly, ψ_A; for the nucleus by itself, characterized by J_C, M_C in the final state, we write ψ_C; for the two electrons in the continuum state we write ψ_1, ψ_2 (orbital functions) and χ_1, χ_2 (spin functions).

The next step is the familiar one of applying the principle of angular momentum conservation to the transitions $A \to B \to C$, and using the standard results for the vector addition of commuting angular momenta. By this means ψ_A is expressed in terms of the ψ_C, ψ_1, ψ_2, χ_1, χ_2, the formula being similar to (13) of § 2(i) but rather more complicated as we now have spin functions for both electrons instead of only one. The argument leading from this formula to the expression for $I(\theta)$ corresponding to (15) does not differ essentially from the argument of § 2(i). It gives us (with the z-axis in the emission direction of the first electron):

$$I(\theta) \sim \sum_{\substack{M_A', M_B', m_{s_1}, m_{j_2}' \\ M_C, m_{s_2}, m_{l_2}}} \left| C^{J_A' M_A'}_{J_B' M_B' j_1 m_{s_1}} C^{J_B' M_B'}_{J_C M_C j_2 m_{j_2}} C^{j_2 m_{j_2}}_{l_2 m_{l_2} s_2 m_{s_2}} \chi_1 \chi_2 Y_{l_2, m_2}(\theta, 0) \right|^2 \quad \ldots\ldots(33)^*$$

To make any further progress with (33) we must consider the relative magnitudes of the four possible values of $|\chi_1(s_1, m_{s_1})\, \chi_2(s_2, m_{s_2})|^2$ corresponding to: $m_{s_1} = \frac{1}{2} = m_{s_2}$; $m_{s_1} = \frac{1}{2} = -m_{s_2}$; $m_{s_1} = -\frac{1}{2} = -m_{s_2}$; $m_{s_1} = -\frac{1}{2} = m_{s_2}$. As pointed

* We have omitted the factor $|C^{j_2 m_{s_2}}_{l_2 0 s_2 m_{s_2}}|^2$ since, as mentioned in § 2 (i), it is the same whether m_{s_2} be $\pm\frac{1}{2}$. Owing to its dependence on j_1 it must be included in the weight factor G_j, which will be introduced when summing over j_1.

out in §2(i), we are not concerned with extra-nuclear fields strong enough to cause appreciable alignment of electron spins, therefore $|\chi_1|^2$ is the same whether m_{s_1} be $\pm\frac{1}{2}$, and $|\chi_2|^2$ the same whether m_{s_2} be $\pm\frac{1}{2}$. If we further assume that the spins of the electrons in the continuum state are just as likely to be parallel as antiparallel* it is clear that all four possible combinations of the numerical values of m_{s_1}, m_{s_2} are equally likely. This means that in (33) $|\chi_1\chi_2|^2$ may be taken outside the summation over m_{s_1}, m_{s_2} and, being independent of the other summation variables, it may be dropped altogether as a constant factor. The expression for $I(\theta)$ then becomes, on finally introducing the summations over J_A', J_B', j_1, j_2:

$$I(\theta)\sim \sum_{\substack{J_A',J_B',\\ j_1,j_2}} \sum_{\substack{M_A',M_B',m_{s_1}\\ M_C,m_{j_2},m_{l_2},m_{s_2}}} G_{j_1}G_{j_2}|C^{J_A'M_A'}_{J_B'M_B'j_1m_{s_1}} C^{J_B'M_B'}_{J_CM_Cj_2m_{j_2}} C^{j_2m_{j_2}}_{l_2m_{l_2}s_2m_{s_2}} Y_{l_1\,m_{l_1}}(\theta,0)|^2 \quad \ldots\ldots(34)$$

The weight factors G_{j_1}, G_{j_2} depend respectively on the matrix elements for transitions to the alternative final states $j_1=l_1\pm\frac{1}{2}$ and $j_2=l_2\pm\frac{1}{2}$; even for low energy transitions these matrix elements must be calculated on the basis of Dirac, rather than Pauli theory, for the reason mentioned in §2(ii). G_{j_1} also includes the factor $|C^{j_1m_{s_1}}_{l_1 0 s_1 m_{s_1}}|^2$. The relative weighting for the different J_A', J_B' in (34) is automatically taken care of by the summations over the magnetic sub-states M_A', M_B'.

(ii) *Discussion*

Expression (34), like (16), represents an angular distribution which is symmetrical about the z-axis and the equatorial plane. It is clear, as previously, that $I(\theta)$ could by a suitable choice of z-axis be expressed in terms of $|Y_{l_1,m_{l_1}}(\theta,0)|^2$ instead of $|Y_{l_2,m_{l_2}}(\theta,0)|^2$, so the highest power of $\cos^2\theta$ appearing in (34) cannot exceed the lower of l_1 and l_2. In terms of multipole orders this means (cf. equations (29) to (32)) that the highest power of $\cos^2\theta$ cannot exceed one plus the order of the lower multipole transition of the cascade.

The numerical application of (34) would in general be very laborious; even when $J_A=J_C=0$ it does not come down to a particularly simple form, in contrast to (16) which, we saw, gives $I(\theta)\sim|Y_{J_B,0}(\theta,0)|^2$ for this case (cf. §2(i)). An expansion of (34) into $Y_{k,0}(\theta,0)$ could of course be made, and may on occasion prove a more useful form, but in general the coefficients in the expansion cannot be simplified by the methods used in dealing with (16) (and with (10) of I) and a term-by-term summation of products of C's would appear unavoidable. In view of this one should probably consider, when dealing with some particular magnetic–magnetic cascade, whether the more general papers of Fierz and of Berestetzky do not, after all, lead less laboriously to a numerical result. In any case it seems likely that the limit of usefulness of the present treatment has been reached in this section. However, it was worth investigating how far this treatment could be pushed, for in the case of electric–electric and magnetic–electric cascades it certainly leads more directly to numerical results than do the general papers.†

* This assumption will be discussed in § 4 and shown to be a good approximation provided Z is not too low, and the life-time of the intermediate nuclear state is not too short.

† *Note added in proof.* Since the above was written, another general paper by Falkoff and Uhlenbeek (*Phys. Rev.*, 1950, **79**, 323) has appeared. This is better adapted for the investigation of particular cases than either the Fierz or Berestetzky papers.

§ 4. LIMITATIONS OF PRESENT TREATMENT

The results of the present paper are valid only within the limits of the various simplifying assumptions introduced in the course of the treatment. It is the purpose of this section to estimate the severity of these limitations. Assumption (*a*) of § 1 imposes an upper limit on the life-time τ_B of the intermediate nuclear state: $\mathbf{J}_B$ must not have time to change its orientation in the interval between the ejection of the first electron and the second. In general the most important influence tending to change M_B (z-component of $\mathbf{J}_B$) is the magnetic interaction between the nucleus and the electrons of the same atom. This has been examined by Hamilton (1940, p. 128) in connection with γ–γ correlation. He relates the Larmor precession period of $\mathbf{J}_B$ in the electronic field to the hyperfine splitting $\Delta\nu$ of the electronic energy levels, due to nuclear interaction, and concludes that for $\Delta\nu \leqslant 1\ \mathrm{cm}^{-1}$ (which is usually true) the mean time for M_B to change by one unit is greater than 3×10^{-11} sec. Thus, in the presence of magnetic interaction between the atomic electrons and the nucleus, assumption (*a*) sets an upper limit of about 10^{-12} sec. to τ_B: essentially the condition is that the nuclear energy level B should be sufficiently broad to make the electronic hyperfine structure unobservable. If the magnetic field of the atomic electrons were neutralized in some way the limiting life-time would be much longer, being now set by the precession period of $\mathbf{J}_B$ in the field of neighbouring nuclei: in an example given by Bloch (1946) this period is about 10^{-4} sec. There are, indeed, substances in which the electronic spin moments are all paired off and the orbital moments which may be present in the free atoms or molecules are quenched because of intermolecular action. However, even for an atom of such a substance it must be remembered that after the ejection of the first electron from an inner shell the pairing off of spins will be destroyed, so that magnetic interaction with the nucleus will still impose an upper limit of about 10^{-12} sec. on τ_B. Thus in substances of this kind the limit on τ_B for conversion–conversion correlation is much more severe than for γ–γ correlation when there is no internal conversion, for in the latter case one knows that if the electronic magnetic moments are balanced out initially they will remain so throughout, and the limit on τ_B will be set by the intra-nuclear field.

Assumption (*b*) of § 1 implies that a conversion electron on its way out of the atom does not communicate any of its angular momentum to the orbital electrons which do not take part in the internal conversion. The probability of a transition in which such a momentum transfer does take place is of the order $(E_S/E_T)^2$, where E_S is the electrostatic interaction energy between the electrons (a few volts) and E_T is the kinetic energy of the conversion electron (10–100 kilovolts, say).* Thus, at worst, we are neglecting an event which happens to only about one in every million conversion electrons.

The limitations imposed by assumption (*c*)—that the conversion electrons come from an initial s-state—were discussed in I for the case of electric transitions. For magnetic transitions the same considerations apply: our treatment is restricted to conversion in the K-shell, and to those cases where conversion in the other shells is predominantly by s-electrons. It is not easy to assess the commonness or rarity of these latter cases†; in any individual case the relative contributions of the

* If the energy is too low the conversion electrons are experimentally undetectable, if it is too high the non-relativistic approximation is invalidated.

† An individual s-electron, with its smaller mean distance from the nucleus, has—barring special selection rules— a greater probability of internal conversion than an individual p-, d-, etc. electron; but in spite of this the latter electrons, being more numerous, may well contribute significantly, even principally, to the total conversion coefficient of the shell.

s-electrons on the one hand, and the p-, d-, etc., electrons on the other to the internal conversion coefficient would have to be worked out for the Z, $h\nu$ and multipole order of that particular transition, also bearing in mind any special selection rules which may apply. Formulae enabling this to be done for the L-shell (for both magnetic and electric transitions, and for Z not greater than 50) have been given by Hebb and Nelson (1940).

The restriction of the whole treatment to non-relativistic energies, by assumption (*d*), probably does not greatly affect the practical interest of this work. At high energies internal conversion is itself a small effect, and the coincidence-rate of successive conversion electrons, being of necessity an effect one order smaller, would scarcely be susceptible to accurate measurement. Correlation between the successive γ-quanta themselves is likely to prove a more useful tool for investigating the angular momenta of nuclear levels in high energy transitions. In § 2 we have made the non-relativistic approximation of neglecting spin interaction for electric multipole internal conversion: this approximation was discussed in I, and shown to be justified by the calculations of Taylor and Mott (1932).

To complete this discussion of the limitations introduced by the simplifying assumptions we consider under what circumstances the spins of the ejected electrons are just as likely to be parallel as antiparallel, which was the assumption introduced in § 3(i) to justify the omission of $|\chi_1 \chi_2|^2$. We first observe that if the assumption is valid for the final (continuum) states of the two conversion electrons it is also true of their initial states, whether or not the z-component of the spin-vector changes sign under internal conversion (so-called 'spin reversal'). Now if the initial states of the two electrons belong to two different shells their spins can, certainly, just as well be parallel as antiparallel. It might be thought that, likewise, if they both belong to the same shell their spins can only be antiparallel, by the Pauli principle; but it must be remembered that during the interval between the ejection of the first electron and the second (i.e. during the nuclear lifetime τ_B) there is a certain probability that the place in the shell vacated by the first electron will be filled by an electron from a higher-energy shell. If such a refilling does occur before ejection of the second electron, the latter will as likely as not be the electron which entered from another shell, i.e. the spin of the second ejected electron will as likely as not be parallel to the spin of the first. The importance of this 'refilling' effect obviously depends on the life-time τ_e of the appropriate electronic transition compared with τ_B. It can be shown that τ_e varies as Z^{-4} (Heitler 1947) so that if Z is not loo low and τ_B is not too short the refilling effect will ensure that, to a good approximation, the spins of the two ejected electrons are just as likely to be parallel as antiparallel. With $\tau_B \sim 10^{-12}$ sec. (the upper limit set by assumption (*a*)) the critical value of Z for the L-shell $\rightarrow$ K-shell transition is about 10: for lower Z than this it is no longer a good approximation to take $\tau_e \ll \tau_B$ and there is an appreciable probability that the refilling of the K-shell does not have time to occur in the interval between the ejection of the first electron and the second.

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Complete Molecular Orbital Treatment of the System H_4

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ABSTRACT. A complete molecular orbital calculation has been made for the linear system of four protons with four associated electrons. Results indicate the validity of the assumptions usually made in approximate calculations of this type. All the three- and four-centred integrals usually neglected in such work have been evaluated and found to be of great importance in determining the energy levels of the system.

§ 1. INTRODUCTION

At present two theoretical methods are known for discussing the properties of metals, that which uses Bloch-type wave functions (Bloch 1928) for the metallic or conduction electrons, and that based on the more recent ideas of Pauling (1938, 1947) who extends the notion of resonating valence-bonds commonly used in molecular theory. The use of Bloch functions is analogous to the molecular orbital (m.o.) technique, the alternative to the Heitler–London–Slater–Pauling method for treating molecular properties; indeed m.o. methods for molecules correspond to the 'tight-binding' approximation (Mott and Jones 1936) for metals. Some connection must exist between the two theories.

The Bloch method (Wigner and Seitz 1933, 1934) seems to give its best results for the alkali metals, where on the average each atom contributes one conduction

electron to the whole. For copper, the predictions (Fuchs 1935) are not so accurate for the heat of sublimation as in the case of the alkalis, although the calculated lattice-constant is quite good. Now in the Bloch method each conduction electron is supposed to move in the potential field of all the ions, plus the time-average field of all the other conduction electrons. The fact that any two electrons are unlikely to be near each other, by reason of both charge and spin, is dealt with after the main body of the calculations has been completed, by a number of small corrections. This assumption about the nature of the effective potential field is usual in calculations on both metals and molecules. It would be of interest, then, if some more direct method of taking inter-electronic repulsions into account could be developed. This might indicate the degree of validity of the usual approximations.

Recently several refined m.o. calculations have been made (e.g. Jacobs 1949, Craig 1950) for various systems, the object being to improve the method so that the predictions it makes for the properties of the excited states of molecules may be as good as those for ground-state phenomena, which are usually in close agreement with experiment. Those refinements have generally involved the construction of configuration wave functions; the electronic interactions can then be taken into account explicitly in the Hamiltonian.

Any allowed allocation of the electrons to the various m.o. levels is called a configuration. By the Pauli principle, a many-electron wave function must be antisymmetrical in the coordinates of the electrons, so that the configurational wave functions will be determinants or sums of determinants whose elements are the simple m.o. functions combined with suitable spin factors. The energies of these configurations are then determined by use of the complete (but spin-independent) Schrödinger Hamiltonian of the system. This stage may be called the approximation of configurations.

In general, the configurations will fall into classes within which they have equivalent symmetry and multiplicity. Since the configurational wave functions are not true eigenfunctions of the Hamiltonian (which contains the inter-electronic distances) but have merely been constructed by an approximate method, non-zero interaction energies will usually exist between those of any one class. This means that a better description of the system under consideration will be obtained by taking as new wave functions linear combinations of the configurational wave functions, and minimizing the energy with respect to the new coefficients thus introduced. The functions so obtained may be taken to represent the stationary states of the system. Thus a state is regarded as a superposition of configurations. As more configurations are taken into account, the resulting state-function approaches the true state-function of the system, i.e. if $E_1, E_2, \ldots E_n$ are the least energies corresponding to the superposition of 1, 2, $\ldots . n$ configurations, then $E_1 > E_2 > \ldots . > E_n > \mathscr{E}_0$, where $\mathscr{E}_0$ is the energy of the true ground-state.

This extended m.o. method will here be applied to a simple model of a metal. Hoffman and Kónya (1948) have shown that metal-like properties emerge from an application of simple m.o. methods to a system consisting of a straight line of atoms each of which contributes one mobile electron to the whole. However, they used a very simplified Hamiltonian, and did not take into account any possible interactions of the ground configuration of their system with ' excited ' configurations. Further, it has been customary (but see, for example, London 1945) in m.o.

calculations to neglect the three- and four-centred integrals which arise in the formulae for the energy. Craig (1950) concludes that these integrals may be important in discussing the energies of π-electrons in benzene; Roothaan and Parr (1949) state that their inclusion leads to much improved agreement with experimental spectral data.

Ideally, we should like to consider, as did Hoffman and Kónya, a linear system of N atoms, and apply the extended theory generally, obtaining the energy as dependent upon N. We have made some calculations for particular N's, and found unexpected results (e.g. what would appear on the simple m.o. basis to be the ground level was in one case *more* energetic in the approximation of configurations than one of the apparent excited levels) unless all these higher integrals were included. We have therefore thought it profitable to make a complete calculation for the simplest possible system in which the effects of configurational interaction and the importance of these integrals may be demonstrated, viz. the system of four protons in a straight line, with four electrons. The results obtained will serve as an indication of what is to be expected when these methods are applied to longer systems.

§2. DETAILS OF CONFIGURATION APPROXIMATION

Let the four protons be labelled a, b, c, d, spaced at equal intervals R, and the coordinates of the electrons be represented by the numerals 1, 2, 3, 4. We shall ignore all possible variations in R. Then $\psi_a(\nu)$ will denote an atomic orbital (a.o.) of the coordinates of electron ν based on nucleus a. The a.o.'s used in the present treatment will simply be hydrogen 1s functions, $\psi_a=(\pi a_0^3)^{-1/2}\exp(-r_a/a_0)$ where $a_0=\boldsymbol{h}^2/4\pi^2\boldsymbol{me}^2$. No screening constant will be used in the a.o.'s. There is some justification for this in that Coulson (1937) has shown in the case of the H_2 molecule, for which the allowed m.o.'s are $\mathrm{I}=(\psi_a+\psi_b)(2+2S)^{-1/2}$ and $\mathrm{II}=(\psi_a-\psi_b)(2-2S)^{-1/2}$, where $\psi=(c^3/\pi)^{1/2}\exp(-cr)$, c being a variation parameter and S the overlap integral, that the best c-value for I is $c>1$ and for II is $c<1$; further, Coulson and Fischer (1949) in a configurational-interaction treatment of the H_2 molecule have shown that the energy curves are not significantly altered by small departures of c from unity, and that the amount of interaction is almost independent of the choice of screening constant. Good agreement with experiment is obtained by use of 1s a.o.'s only.

There will be four possible m.o.'s of the form $\sum_{s=a}^{d} x_s\psi_s$. These will be denoted by i, j, k, l and it will be supposed that the increasing order of the corresponding energies is lexical. This means that on the simple m.o. picture the configuration of lowest energy will be $\mathrm{i}^2\mathrm{j}^2$. Also i and k will be symmetrical (σ_g) with respect to reflection in the plane normal to the line of protons at its geometrical midpoint, while j and l will be antisymmetrical (σ_u). We fix the various sets of coefficients x_s by the usual m.o. methods, making the assumption (see, for example, Coulson and Chirgwin 1950, Mulliken 1948) in order to solve the secular equations, that $\beta_2/\beta_1=S_2/S_1$, $\beta_3/\beta_1=S_3/S_1$, β_1, β_2, β_3 being the resonance integrals between a.o.'s based on nearest, second nearest, and third nearest neighbours, and S_1, S_2, S_3 the corresponding overlap integrals $\int\psi_r\psi_s d\tau$, $r\neq s$; these last are tabulated in the Appendix for values of the distance $r-s$ chosen for reasons stated below. The coefficients x_s are shown in Table 1; i, j, k, l are then orthonormal.

We now construct the configuration functions $\phi_n \equiv \phi_n(1234)$. These will be determinants, or sums of determinants, each of which may be denoted by its leading diagonal, so that for instance

$$\phi_0 \equiv \phi(i^2j^2) = |\,i(1)\alpha(1)i(2)\beta(2)j(3)\alpha(3)j(4)\beta(4)\,|$$
$$\equiv (4!)^{-1/2}\begin{vmatrix} i(1)\alpha(1) & i(1)\beta(1) & j(1)\alpha(1) & j(1)\beta(1) \\ i(2)\alpha(2) & i(2)\beta(2) & j(2)\alpha(2) & j(2)\beta(2) \\ i(3)\alpha(3) & i(3)\beta(3) & j(3)\alpha(3) & j(3)\beta(3) \\ i(4)\alpha(4) & i(4)\beta(4) & j(4)\alpha(4) & j(4)\beta(4) \end{vmatrix}$$

α and β being spin functions.

Rearrangements of the type $i^2j^2 \rightarrow i^2jl$ give rise to singlet and triplet configurations, with wave functions of the type

$$\phi(i^2jl) = (2.4!)^{-1/2}[\,|\,i(1)\alpha(1)i(2)\beta(2)j(3)\alpha(3)l(4)\beta(4)\,|$$
$$\pm\,|\,i(1)\alpha(1)i(2)\beta(2)j(3)\beta(3)l(4)\alpha(4)\,|\,]$$

the upper sign referring to the triplet configuration with $S_z = 0$, the lower to the singlet. $i^2j^2 \rightarrow i^2k^2$ leads to a singlet whose wave function is of the same form as that of the lowest configuration. $i^2j^2 \rightarrow ijkl$ leads to one quintet, three triplets and two singlets. The energies of all these are found by means of the Hamiltonian

$$\mathscr{H} = \frac{-\hbar^2}{8\pi^2 m}\sum_{\nu=1}^{4}\nabla_\nu^2 + \sum_{\text{abcd}}\sum_{\nu=1}^{4}\frac{-e^2}{r_{a\nu}} + \sum_{\mu<\nu}\frac{e^2}{r_{\mu\nu}} = \sum_\nu H(\nu) + \sum_{\mu<\nu}\frac{e^2}{r_{\mu\nu}} \qquad \ldots\ldots(1)$$

μ and ν denoting electrons, and e the electronic charge. The configuration energies $\int \phi_n \mathscr{H} \phi_n \, d\tau$ can then be expressed in terms of the integrals ϵ, γ, δ, where

$$\epsilon_s = \int s(\nu)H(\nu)s(\nu)\,d\tau_\nu \qquad \ldots\ldots(2)$$

$$\gamma_{st} = \int\int |\,s(\mu)\,|^2(e^2/r_{\mu\nu})\,|\,t(\nu)\,|^2\,d\tau_\mu\,d\tau_\nu \qquad \ldots\ldots(3)$$

$$\delta_{st} = \int\int s(\mu)t(\mu)(e^2/r_{\mu\nu})s(\nu)t(\nu)d\tau_\mu\,d\tau_\nu \qquad \ldots\ldots(4)$$

where s and t can be i, j, k or l.

Thus
$$\left.\begin{aligned} {}^1E(i^2j^2) &= 2\epsilon_i + 2\epsilon_j + \gamma_{ii} + \gamma_{jj} + 4\gamma_{ij} - 2\delta_{ij} \\ {}^1E(i^2jl) &= 2\epsilon_i + \epsilon_j + \epsilon_l + \gamma_{ii} + \gamma_{jl} + 2\gamma_{ij} + 2\gamma_{il} - \delta_{ij} - \delta_{il} + \delta_{jl} \\ {}^3E(i^2jl) &= {}^1E(i^2jl) - 2\delta_{jl} \end{aligned}\right\} \qquad \ldots\ldots(5)$$

the superscript preceding the energy symbol denoting the multiplicity of the configuration. The ϵ's, γ's and δ's may now be expanded into sums of energy-integrals over a.o.'s. We may take a_0 as our unit of length and express all distances in terms of it. We shall assume that $R = 1{\cdot}4a_0$, which is the equilibrium internuclear separation in H_2. Coulson and Fischer (1949) have shown that the usual m.o. methods are applicable at this distance. The required atomic integrals are of the following types:

$$\text{1-electron: } (m;np) = \frac{1}{\pi}\int \frac{1}{r_m}\exp\{-(r_n + r_p)\}\,d\tau, \quad S_{mn} = \frac{1}{\pi}\int \exp\{-(r_m + r_n)\}\,d\tau$$

where r_m is the distance of the electron from nucleus m, etc., and m, n, p may be any of a, b, c, d, the case m = n = p not being needed. The two-centred integrals

(m; nn) and (m; mn) which are quite simple were first evaluated by Heitler and London (1927). The various three-centred integrals are special cases of K(n; ij) in the notation of Hirschfelder, Eyring, and Rosen (1936). All these integrals may be obtained by use of ellipsoidal coordinates based on two of the nuclei as foci.

$$\text{2-electron: } (\text{mn, pq}) = \frac{1}{\pi^3}\iint \exp\{-(r_{m1}+r_{n1}+r_{p2}+r_{q2})\}\frac{d\tau_1\, d\tau_2}{r_{12}}$$

where r_{m1} is the distance of electron 1 from nucleus m, etc., r_{12} = inter-electronic distance, and m, n, p, q may be any of a, b, c, d.

The one-centred integral (mm, mm) and the two centred integrals (mm, nn) and (mm, mn) may be easily obtained by use of the expressions for (m; nn) and (m; mn) in the integrations over the coordinates of one of the electrons. (mn, mn) was first obtained by Sugiura (1927). Formulae for the three-centred integrals (mm, np) are obtainable from the above paper of Hirschfelder, Eyring and Rosen, but it was not found practicable to use their formulae for (mn, mp). All these latter three-centred integrals, and also the four-centred integrals (mn, pq) were evaluated from formulae (which are to appear elsewhere) kindly provided by M. P. Barnett. In these formulae the integrals were obtained as convergent infinite series involving integrals of the so-called $\zeta(\beta, r; \rho)$ functions (Coulson and Barnett 1951). The numerical values of all integrals are appended to this paper. From them we obtain the following values of the molecular integrals (all in electron volts):

$\gamma_{ii} = 12{\cdot}933$	$\gamma_{ij} = 11{\cdot}508$	$\delta_{ij} = 3{\cdot}560$	$\epsilon_i = -55{\cdot}392$
$\gamma_{jj} = 12{\cdot}016$	$\gamma_{ik} = 12{\cdot}657$	$\delta_{ik} = 2{\cdot}347$	$\epsilon_j = -45{\cdot}733$
$\gamma_{kk} = 13{\cdot}360$	$\gamma_{il} = 15{\cdot}010$	$\delta_{il} = 1{\cdot}773$	$\epsilon_k = -37{\cdot}360$
$\gamma_{ll} = 14{\cdot}370$	$\gamma_{jk} = 12{\cdot}534$	$\delta_{jk} = 2{\cdot}788$	$\epsilon_l = -20{\cdot}842$
	$\gamma_{jl} = 15{\cdot}762$	$\delta_{jl} = 0{\cdot}366$	
	$\gamma_{kl} = 8{\cdot}722$	$\delta_{kl} = 1{\cdot}278$	

It is seen at once that all the γ's are roughly equal, as are all the δ's, whilst the ϵ's are nearly in arithmetic progression.

The first fact means that the differences between configuration energies will be *mainly* due to the different ϵ's involved. Hence the second fact implies that configurations i^2k^2, ij^3k will have nearly equal energies, as will ijk^3, i^2kl and other cases which might be cited. We may expect interaction between such approximately equi-energetic configurations to be important in determining molecular states; but this depends also on the inter-configurational energy matrix-elements, whose magnitudes cannot in general be foreseen.

If to $\mathscr{H}$ we add the constant term $(13/3)(e^2/R) = 83{\cdot}798$ ev. due to the mutual potential energy of the protons, we obtain absolute energies for the system, in the approximation of configurations. Those listed in Table 2 cover a range of more than 50 ev. relative to the lowest configuration i^2j^2. We distinguish the various (ijkl) configurations by superfixes referring to the multiplicity, and suffixes increasing in order of energy.

Since the ground configuration has an energy of $-54{\cdot}591$ ev. we see that our system is stable against dissociation into four H-atoms, which would have a combined energy of $-54{\cdot}150$ ev., but not against dissociation into two H_2 molecules, which would have a combined energy of $-60{\cdot}37$ ev. Hirschfelder, Eyring and

Rosen (1936) quote an experimental value of -103 kcal/mole for the symmetrical H_3 molecule. This means that the energy of the system H_3+H would be $-58{\cdot}61$ ev., which falls below that of our system. Configurational interaction will lower our figure, but we see already that wave functions built from 1s a.o.'s yield a reasonable energy value.

§3. CONFIGURATIONAL INTERACTION

The question of interaction between these configurations must now be investigated. Were the configuration functions the best description of the system obtainable by methods based on m.o.'s, the energy matrix-elements between different configurations would vanish. In fact, these quantities are found to be of the same order of magnitude as the δ's. Since some configurations are separated by energy-differences of just this order, we may expect interaction between them to be important, although the effect on the ground configuration may be slight, since the nearest configuration with which it can interact is distant 22·93 ev. in energy.

Let
$$\eta_{xy} = \int \mathrm{x}(\nu) H(\nu) \mathrm{y}(\nu)\, d\tau_\nu \qquad \ldots\ldots(6)$$

$$\zeta_{xy}{}^{zw} = \iint \mathrm{x}(\mu)\mathrm{y}(\mu)(e^2/r_{\mu\nu})\mathrm{z}(\nu)\mathrm{w}(\nu)\, d\tau_\mu\, d\tau_\nu \qquad \ldots\ldots(7)$$

where x, y, z, w may be any of i, j, k, l. With this notation δ_{st} becomes $\zeta_{st}{}^{st}$. The interaction energy between i^2jl and ij^2k (singlets) may be written

$$\int \phi(i^2jl)\mathscr{H}\phi(ij^2k)\, d\tau. \qquad \ldots\ldots(8)$$

All possible $\int \phi_n \mathscr{H} \phi_m\, d\tau$ can then be expressed in terms of the η's and ζ's, e.g. for configurations in the class $^1\Sigma_g$:

$$\int \phi(i^2j^2)\mathscr{H}\phi(i^2k^2)\, d\tau = \zeta_{jk}{}^{jk}$$

$$\int \phi(i^2j^2)\mathscr{H}\phi(i^2jl)\, d\tau = \sqrt{2}(\eta_{jl} + \zeta_{jj}{}^{jl} + 2\zeta_{ii}{}^{jl} - \zeta_{ij}{}^{il})$$

$$\int \phi(i^2jl)\mathscr{H}\phi(ij^2k)\, d\tau = 2\zeta_{ik}{}^{jl} - \zeta_{ij}{}^{kl}$$

$$\int \phi(i^2jl)\mathscr{H}\phi(k^2jl)\, d\tau = \zeta_{ik}{}^{ik}$$

$$\int \phi(i^2k^2)\mathscr{H}\phi(i^2jl)\, d\tau = \sqrt{2}\zeta_{kj}{}^{kl}$$

$$\int \phi(i^2k^2)\mathscr{H}\phi(ij^2k)\, d\tau = -\sqrt{2}\zeta_{ji}{}^{jk}$$

$$\int \phi(i^2j^2)\mathscr{H}\phi(k^2l^2)\, d\tau = 0.$$

Terms involving $\phi(ijkl)$ may be written down similarly, but are rather cumbersome. All the η's and ζ's can be expanded as were the ϵ's, γ's, and δ's into linear combinations of the same integrals over a.o.'s. It is found that the various interaction energies may be positive or negative in sign, but all lie in the range ± 5 ev. We can now use these results to determine the wave functions of the energy states of the system, these being linear combinations of the configurational functions :

$$\Psi_t = \sum_n C_n{}^t \phi_n \qquad \ldots\ldots(9)$$

where the $C_n{}^t$ are to be found by minimizing the energy function

$$E_t = \left(\int \Psi_t \mathscr{H} \Psi_t\, d\tau\right) \Big/ \left(\int \Psi_t{}^2\, d\tau\right)$$

with respect to the C_n^t. $(C_n^t)^2$ is the weight with which configuration n enters state t; n will always refer to a configuration, t to a state. This leads to the usual determinantal equation for the E_t whence the various C_n^t may be found. As many ϕ_n can be included in (9) as is convenient; in practice we have found that the difference between including the lowest five or six in any class is very small so far as the lowest E is concerned. Using the $^1\Sigma_g$ configurations listed in Table 2 we find the E_t values listed in Table 3. We see that the only energies much affected by interaction are those deriving from ij^2k and i^2k^2, which lie rather close together in the configuration approximation. The ground configuration is of course slightly stabilized. These results are reflected in the values of $(C_n^t)^2$ (Table 3).

It should be noted that the E_t decrease in reliability as E_t increases. The ground energy would probably not be appreciably affected by the inclusion of more than six configurations, but the higher states would all be altered slightly.

We see that for our system configurational interaction is of little importance in determining the ground energy, but must be taken into account in discussion of 'excited' states. Similar calculations may be made for the $^1\Sigma_u$, $^3\Sigma_g$ and $^3\Sigma_u$ classes and similar results obtained: the lowest energy in each class is lowered by at most 1·5 ev., 'excited configurations' lying close together in energy give rise to more separated states, and one configuration is usually dominant in each state.

§4. CHARGE DISTRIBUTION

If we integrate ϕ_n^2 over the coordinates of all electrons but one, say electron 1, we obtain a function which we may suppose to be proportional to the charge-density in configuration n due to electron 1. Thus

$$\iiint [\phi(i^2j^2)]^2 \, d\tau_2 \, d\tau_3 \, d\tau_4 = \tfrac{1}{2}[i^2(1) + j^2(1)] \qquad \ldots\ldots(10)$$

Now

$$i^2(1) = \sum_{r=a}^{d} (x_r^i)^2 \psi_r^2(1) + \sum_{r=a}^{d} \sum_{s \neq r} x_r^i x_s^i \psi_r(1) \psi_s(1) \qquad \ldots\ldots(11)$$

It is now reasonable to define the quantity q_r^i given by the equation

$$q_r^i = (x_r^i)^2 + \sum_{s \neq r} x_r^i \chi_s^i S_{rs} \qquad \ldots\ldots(12)$$

where S_{rs} is the overlap integral between a.o.'s based on nuclei r and s, as being the mean electronic charge associated with nucleus r due to the occupation of orbital i by one electron. Summing over the occupied orbitals which constitute any given configuration n say, with a factor 1 or 2 according as the orbital is singly or doubly occupied, we obtain the quantity

$$Q_r^n = \sum_i p_i q_r^i \qquad (p_i = 1 \text{ or } 2) \qquad \ldots\ldots(13)$$

which may be called the mean electronic charge at nucleus r when the system is in configuration n. We may extend this convention to the final state approximation, i.e. form the function

$$P_t(1) = \iiint \Psi_t^2 \, d\tau_2 \, d\tau_3 \, d\tau_4. \qquad \ldots\ldots(14)$$

It is found that $P_t(1)$ when expanded contains the cross terms $i(1)k(1)$ and $j(1)l(1)$ as well as the $i^2(1)$ etc. which occur in the configuration approximation. Using the developments (11) (12) (13) of $i^2(1)$ and the corresponding developments of these cross terms we can obtain the quantities $\bar{Q}_r^t$, the mean electronic charge

at nucleus r when the system is in state t. Some Q_r^n and $\overline{Q}_r^t$ are recorded in Table 4. Since from symmetry considerations nuclei a, b will have the same mean charges as d, c respectively, only the cases r = a, b are tabulated.

It is seen that the general effect of configurational interaction is to distribute the charge more evenly among the nuclei. There does not seem to be any correlation between the pattern of the charge distribution and the energy, i.e. there is no marked accumulation of charge at any part of the system as it becomes more energetic. The above definition of Q_r^n is equivalent to that used in the simple m.o. theory when all overlap integrals are included (Coulson and Chirgwin 1950). Since Q_r^n and $\overline{Q}_r^t$ are merely defined quantities we should not expect them to correspond exactly to anything of physical significance; but for a state where $\overline{Q}_a^t > \overline{Q}_b^t$ e.g. the ground state, we could take this as meaning that the average electron density near the ends of the system in state t is greater than in the middle.

§ 5. THE FOCK M.O. METHOD

The m.o.'s i, j are not the best possible pair by which to describe the ground configuration. In any system for which the coefficients in the linear combinations of a.o.'s are not completely determined by symmetry requirements, we might hope to reduce configurational interaction by choosing the coefficients by a method different from that of the simple m.o. theory which uses an approximate Hamiltonian. Such a procedure for our present system is to assume

$$i' = I'(\lambda'\psi_a + \psi_b + \psi_c + \lambda'\psi_d), \quad j' = J'(\mu'\psi_a + \psi_b - \psi_c - \mu'\psi_d)$$

I' and J' being normalizing factors; use the determinantal wave-function $|i'(1)\alpha(1)i'(2)\beta(2)j'(3)\alpha(3)j'(4)\beta(4)|$ and the complete Hamiltonian $\mathscr{H}$; construct the energy $E(i'^2j'^2)$ of the lowest configuration as a function of λ' and μ'; find the values of λ' and μ' which minimize this function. This is called the 'Fock m.o. method' by Coulson and Jacobs (1951).

To construct wave functions to represent 'excited' configurations, two methods are possible: first, we may assume that i' and j' are not altered by the change from the configuration to some other, that is, that the coefficients in i' and j' for the configuration $i'^2j'l'$, for example, are the same as those for $i'^2j'^2$ and further that these coefficients are not altered between different excited configurations. If this assumption is made it follows that k' and l' are completely determined by the requirement that they be orthogonal to i' and j' respectively. The second, more elaborate, possibility is to assume that the coefficients in such a configuration as, for example, that *formerly* described as i^2jl are to be determined by reference to this configuration alone, or, more explicitly, to assume

$$i'' = I''(\lambda''\psi_a + \psi_b + \psi_c + \lambda''\psi_d)$$
$$j'' = J''(\mu''\psi_a + \psi_b - \psi_c - \mu''\psi_c)$$
$$l'' = L''(\rho''\psi_a + \psi_b - \psi_c - \rho''\psi_d)$$

and minimize $E(i''^2j''l'')$ with respect to λ'', μ'' and ρ'' subject to the condition that l'' be orthogonal to j''. In the first method we apply the Fock procedure to the ground configuration only, in the second, to each configuration separately.

The Fock m.o. method is tantamount to allowing a limited amount of interaction to occur between configurations constructed from the simple m.o.

functions i j k l, and thus will give a ground energy lying between that of the lowest of these latter configurations and that of the lowest state. We may therefore expect interaction between the Fock configurations to be less important than between the old ones. Thus, if we wish to retain the configuration picture of molecular electronic levels, the Fock procedure will give the better energy.

Values for the configuration energies calculated by the (first) Fock method, and the normalized Fock coefficients, are given in Tables 5 and 6. It is seen that although the coefficients are appreciably different from those given by the Coulson–Chirgwin method, the values of the energies are but slightly altered.

The calculations for the Fock m.o. method were done by Dr. J. H. van der Waals, whose cooperation the writer wishes to acknowledge.

§ 6. DISCUSSION AND CONCLUSIONS

We have shown that for our particular system configurational interaction is not of great importance in the determination of the ground energy. This contrasts with the work of Coulson and Jacobs (1951) who in the course of calculations on the energies of the π-electrons in butadiene found interaction to be of great importance. But Coulson and Fischer (1949) found that in the states of the H_2 molecule the weight of the apparent lowest configuration in the ground state was 0·9857, which is only 3% different from (greater than) our value, and that the energy at the equilibrium separation of the nuclei was scarcely affected, though this was not true for larger separations.

A physically reasonable value for our ground energy has been obtained provided no further approximations are made once the initial one-electron wave functions have been set up. Of course, the geometrical arrangement in which the nuclei are equally spaced is unlikely to be that of greatest stability; however, the energy we obtain is an upper limit for the system in equilibrium.

A further improvement would be to include some hydrogenic 2s- and 2p-type functions in the linear combinations of a.o.'s, that is, from a physical point of view to suppose that some atomic excitation contributes to molecular excitation. Again, probably this would alter the excited states more than it would stabilize the ground state. For the H_2 molecule, Rosen (1931) used functions $\psi_{1s}(1)+\sigma\psi_{2p}(1)$ instead of merely $\psi_{1s}(1)$ for the a.o.'s in a Heitler–London treatment, and found that the minimizing value of σ was 0·10; this reduced the ground energy obtained by using only 1s functions by 0·26 ev. Such a step in our case, however, would involve the computation of many more energy integrals.

In Table 4, in the approximation of configurations, it is seen that the mean charges associated with the various atoms often depart considerably from unity. This is not plausible on physical grounds, since presumably the electrons will tend to keep as far apart from each other as the potential field of the nuclei allows. Thus we see in another way that the r_{12} effect obliges us to take interaction between configurations into account; our configurational wave functions alone do not constitute a good description of the system. (In the configurations i^2k^2, j^2l^2 and ijkl the Q_r^n are all exactly unity; this is a mathematical consequence of the definition (12) if the m.o.'s are determined by the methods outlined in § 2.)

Since the γ's and δ's do not vary greatly amongst themselves, we have some justification for the notion that each electron moves in the time-average field of all the others. Our work, then, shows that the assumptions usually made in

calculations which use Bloch-type wave functions are probably not very severe, at least, we may suppose, in systems having one mobile electron per atom.

The importance of the three- and four-centred integrals must not be underestimated. Their neglect leads to the following gross errors: γ_{kl} appear to be negative (a clear absurdity since the integrand is everywhere positive), the ϵ's appear to be in the order $\epsilon_i > \epsilon_j > \epsilon_k > \epsilon_l$ which is just the opposite of that of the exact values quoted above (Crawford and Parr (1949) also find this inversion in a discussion of the electronic energies of the benzene molecule), some of the inter-configurational matrix elements are so altered as to appear with the wrong sign, and the near-equality of the γ's and δ's is destroyed. It is clear that no molecular calculation which has as its object the *absolute* energy values of a system (i.e. the energies relative to that of the infinitely dispersed components) can yield an accurate result unless many more integrals are taken into account than it has hitherto been customary to include.

The magnitudes of the overlap integrals S are noteworthy; for unsaturated hydrocarbon molecules the value of S between atomic 2pz functions based on neighbouring carbon nuclei is usually about 0·25, that between non-nearest neighbours being negligible. In our present problem it is the much larger S-values that necessitate the introduction of Mulliken's assumption in § 2 for the determination of the m.o. coefficients.

We may conclude that our complete calculations lend empirical justification to the assumptions mentioned in § 1, and confirm the use of the method of molecular orbitals as a basis for energy calculations. They also indicate the difficulties to be expected when analogous calculations are made for more complex systems, as then the number of multi-centred integrals which might be quite important would increase rapidly, as would the difficulty of their evaluation.

ACKNOWLEDGMENTS

The writer would like to take this opportunity of thanking Professor C. A. Coulson for suggesting this investigation, and for the interest he has taken in the work at all stages. It was done during the tenure of a Research Grant from the Sir James Caird's Travelling Scholarships Trust. Thanks are also due to the British Iron and Steel Research Association for the provision of a Marchant Calculator on which the numerical work was done. The writer must also thank Mr. M. P. Barnett, of this department, for providing him with formulae and guidance in the evaluation of the multi-centred integrals, which made this work possible.

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APPENDIX

Values of Integrals over Atomic Orbitals

Values are given in electron volts; the conversion factor e^2/a_0 has been taken equal to 27·073 ev. The index p may represent atoms b, c, or d. x is the distance a–p measured in atomic units.

1-electron:

x	(a; pp)	(a; ap)	Sap	(a; bc) = 9·321	(b; ac) = 7·523
1·4	16·516	16·023	0·752943	(a; bd) = 3·840	(b; ad) = 2·655
2·8	9·533	6·256	0·389995	(a; cd) = 5·839	
4·2	6·438	2·111	0·166156		

2-electron: $(aa, aa) = 5e^2/8a_0 = 16·921$

x	(aa, pp)	(aa, ap)	(ap, ap)	(aa, bc) = 8·376	(bb, ac) = 5·722
1·4	13·632	11·530	8·627	(aa, bd) = 3·589	(bb, ad) = 2·113
2·8	9·155	4·998	2·025	(aa, cd) = 5·583	(ab, bc) = 7·475
4·2	6·399	1·786	0·320		(ab, bd) = 3·207
				(ab, ac) = 4·050	(ab, cd) = 5·033
				(ab, ad) = 1·481	(ac, bd) = 1·903
				(ac, ad) = 0·776	(ad, bc) = 1·776

Table 1. M.O. Coefficients (normalized)

	ψ_a	ψ_b	ψ_c	ψ_d
i	0·266765	0·343894	0·343894	0·266765
j	0·635824	0·303608	−0·303608	−0·635824
k	1·056707	−0·819711	−0·819711	1·056707
l	1·121978	−2·349679	2·349679	−1·121978

Table 2. Configuration Energies (ev.)

$^1\Sigma_g$		$^1\Sigma_u$		$^3\Sigma_g$		$^3\Sigma_u$	
i^2j^2	−54·591	i^2jk	−39·401	ij^2k	−36·358	i^2jk	−44·977
ij^2k	−31·664	ijk^2	−18·372	i^2jl	−17·529	ijk^2	−25·492
i^2k^2	−29·479	i^2kl	−11·041	$^3(ijkl)_1$	−10·06	i^2kl	−13·597
i^2jl	−16·797	ij^2l	− 4·489	$^3(ijkl)_2$	− 4·16	ij^2l	− 8·035
j^2k^2	−12·452	ik^2l	2·120	$^3(ijkl)_3$	− 1·66	ik^2l	− 1·426
$^1(ijkl)_1$	− 1·337	j^2kl	9·584				

Table 3. State Energies and Weights of Configurations ($^1\Sigma_g$)

State t	E_t	$(C_n^t)^2$ n=i^2j^2	ij^2k	i^2k^2	i^2jl	j^2k^2	$^1(ijkl)_1$
1	−56·404	0·9515	0·0149	0·0128	0·0152	0·0006	0·0050
2	−36·101	0·0166	0·5674	0·3157	0·0344	0·0659	0·0000
3	−27·603	0·0003	0·3620	0·6008	0·0047	0·0003	0·0319
4	−15·739	0·0167	0·0016	0·0145	0·9060	0·0579	0·0033
5	−11·167	0·0053	0·0282	0·0492	0·0283	0·8229	0·0660
6	0·694	0·0096	0·0252	0·0068	0·0114	0·0535	0·8934

Table 4. Q_r^n and $\bar{Q}_r^t$ for Lower Configurations

$^1\Sigma_g$

n	Q_r^n	r	$\bar{Q}_r^t$	t
i^2j^2	1·190	a	1·171	1
	0·810	b	0·829	
ij^2k	1·314	a	1·183	2
	0·686	b	0·817	
i^2k^2	1·000	a	1·157	3
	1·000	b	0·843	

$^1\Sigma_u$

n	Q_r^n	r	$\bar{Q}_r^t$	t
i^2jk	1·095	a	1·089	1
	0·905	b	0·911	
ijk^2	1·219	a	1·171	2
	0·781	b	0·829	
i^2kl	0·781	a	0·877	3
	1·219	b	1·123	

$^3\Sigma_g$

n	Q_r^n	r	$\bar{Q}_r^t$	t
ij^2k	1·314	a	1·266	1
	0·686	b	0·734	
i^2jl	0·876	a	0·888	2
	1·124	b	1·112	
$^3(ijkl)_1$	1·000	a	0·915	3
	1·000	b	1·085	

$^3\Sigma_u$

n	Q_r^n	r	$\bar{Q}_r^t$	t
i^2jk	1·095	a	1·018	1
	0·905	b	0·982	
ijk^2	1·219	a	1·177	2
	0·781	b	0·823	
i^2kl	0·781	a	0·907	3
	1·219	b	1·093	

Table 5. Fock M.O. Coefficients

	ψ_a	ψ_b	ψ_c	ψ_d
i′	0·19803	0·39607	0·39607	0·19803
j′	0·52956	0·51917	−0·51917	−0·52956
k′	1·07172	−0·79582	−0·79852	1·07172
l′	1·17588	−2·31164	2·31164	−1·17588

Table 6. Fock Configuration Energies (ev.)

$^1\Sigma_g$		$^1\Sigma_u$		$^3\Sigma_g$		$^3\Sigma_u$	
i^2j^2	−55·637	i^2jk	−39·623	ij^2k	−36·752	i^2jk	−45·187
ij^2k	−32·428	ijk^2	−18·099	i^2jl	−19·306	ijk^2	−24·961
i^2k^2	−29·482	i^2kl	−11·012	$^3(ijkl)_1$	−11·001	i^2kl	−13·814
i^2jl	−15·406	ij^2l	− 7·102	$^3(ijkl)_2$	− 3·146	ij^2l	−10·674
i^2k^2	−11·821	ik^2l	2·029	$^3(ijkl)_3$	− 1·670	ik^2l	− 1·563
$^1(ijkl)_1$	− 0·327	j^2kl	7·494			j^2kl	4·957

The Diamagnetic Anisotropy of Large Aromatic Systems Parts I and II

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ABSTRACT.

PART I. A short discussion is given of the magnetic properties of large aromatic hydrocarbons and of the applicability of various wave-mechanical methods of calculating the diamagnetic susceptibility. The ultimate particles of most cokes and carbon blacks are not sufficiently large to be regarded as crystalline and must be treated as large molecules: calculations on certain simple types of molecule are to be carried out with a view to elucidating the effect of particle size and shape on the magnetic properties of such carbons. For systems of these dimensions the molecular orbital method should be valid and, in fact, appears to constitute the only feasible approach to the problem.

PART II. The method of molecular orbitals is applied in a discussion of the diamagnetic anisotropy of the p-polyphenyls, which may be regarded as the simplest type of aromatic chain molecule. An almost perfectly linear relationship is predicted between diamagnetic anisotropy and chain length: in this case the molecular orbital method should be valid for chains of up to at least 2,000 rings. The results are discussed and the desirability of further accurate experimental work on these molecules is pointed out: this would make possible a stringent test of the whole theory.

PART I. GENERAL PRINCIPLES

§1. INTRODUCTION

THE successful correlation of the diamagnetic susceptibilities of many organic molecules by means of Pascal's rules is well known. It is possible to express the mean susceptibility of a saturated organic molecule in the form $\chi_m = \Sigma\chi_a + \lambda$, where the χ_a are the atomic susceptibilities of the component atoms and λ is a 'constitutive correction', depending on the number and type of the various bonds in the molecule. This amounts to saying that $\chi_m = \Sigma\chi_a'$ where χ_a' is the effective susceptibility of each atom, the exact value of χ_a' depending on the immediate environment of the atom.

In dealing with aromatic systems, however, Pascal's rules are of doubtful value. For example, the value of χ_a' which must be assumed for a carbon atom in naphthalene is much greater than for a carbon atom in benzene, although the carbon atoms in both molecules possess essentially similar environments. The constitutive corrections are thus apparently dependent on the size and shape of the whole molecule and Pascal's rules of approximate additivity cease to be useful. On closer examination it appears that aromatic systems are characterized by a high diamagnetic anisotropy, the principal susceptibility normal to the plane of the molecule being very considerably larger than the two approximately equal susceptibilities in the plane. The latter depend in an additive manner on a suitably chosen set of χ_a': it is therefore the high *anisotropy* which must be dependent not simply on local structure but on the shape and size of the whole molecule. Since only the π-electronic orbitals of an aromatic molecule may be regarded as completely non-localized, it is at once evident that the marked magnetic

anisotropy normal to the plane of such a molecule must be associated with these characteristic non-localized molecular orbitals.

This view, which replaces the classical conception of large orbits, is now generally held and some attempts at a quantitative treatment have been made. Pauling (1936) gives a semi-classical treatment assuming the mobile electrons are free to move over the hexagonal network of C—C bonds, the induced mesh currents giving rise to a magnetic shell. F. London (1937) employs a more rigorous quantum-mechanical method, which, however, in spite of being fundamentally more satisfactory, has only been applied to quite small molecules owing to the labour of calculation. In most cases the two methods give essentially similar results and the agreement with experimental figures is very satisfactory. On the other hand, both London (1937) and Squire (1938) criticize Pauling's method because it leads to certain conclusions in contradiction with those obtained quantum-mechanically; it appears, however, that their results are vitiated by errors which have crept into the calculations and that in fact there is no fundamental divergence between the predictions of the two theories. Indeed, a more complete comparison of these methods is very desirable, for if no real disagreements are encountered Pauling's simple method might be applied with greater confidence to complicated systems which resist the more complete treatment.

The present series of papers has arisen in an attempt to elucidate the widely different magnetic properties of various carbon blacks and cokes*. There is evidence to suggest that the ultimate particles in the carbon structure are either single graphite planes or very loosely bound sets of planes, individual planes seldom being very much greater than 100 A. in diameter (see, for example, Blayden, Gibson and Riley 1943, Franklin 1950). Even in 'pure' carbons there is probably sufficient hydrogen present to saturate the edge valencies of such fragments: the structure will therefore be pictured as a random aggregate of plane aromatic molecules of various shapes and sizes, linked only by van der Waals forces.

The dependence of magnetic properties on such features as average particle size and shape, which are themselves determined by the mode of preparation and subsequent treatment of the carbon, is of very great interest; indeed, if an adequate correlation can be made, the magnetic characteristics of a coke might serve as a valuable guide to its ultimate structure.

These papers will be devoted to a study of the magnetic anisotropy of certain typical structures occupying a position intermediate between the very small aromatic systems considered by London, and the infinite graphite sheet. Although there is no evidence to suggest that these structures are actually present in carbons it is highly probable that structures of a rather similar nature are in fact responsible for their characteristic properties. We might for instance broadly distinguish two types of graphite fragment, 'chain structures' and 'condensed structures'; it is of interest to enquire whether this distinction is reflected in the magnetic behaviour of the fragments.

London's treatment is only practicable in the case of large molecules if the secular determinants of molecular orbital theory can either (i) be evaluated analytically, or (ii) be reduced to more manageable dimensions by group theory. In either case there is an obvious limitation to structures of simple or highly symmetrical form. Examples of the two cases are afforded by (i) the polyphenyls and (ii) the systems of hexagonal symmetry such as coronene. A third possibility

* We shall subsequently refer to such materials as 'carbons', a characteristic feature of their structure being the preponderance of carbon atoms in the trigonal valence state.

exists, however: the secular equation in the absence of a magnetic field may be reducible by analytical methods (Rutherford 1945) depending essentially on the existence of symmetries which are destroyed by the field. Examples of the treatment of such systems (for example, the polyacenes) by second-order perturbation theory, using the known eigenvectors of the unperturbed system, will be given later.

§ 2. WAVE FUNCTIONS FOR THE MOBILE ELECTRONS IN A MAGNETIC FIELD

We shall calculate the anisotropic part of the magnetic susceptibility directly by approximate solution of the wave equation for the mobile electrons of a plane aromatic system, with an applied magnetic field normal to the plane of the molecule.

If the field dependence of the energy is expressed by

$$E = E_0 - \tfrac{1}{2}\chi H^2 \qquad \ldots\ldots(1)$$

then χ is the magnetic susceptibility in this direction; if χ is negative the system is diamagnetic. As already indicated, χ so calculated will be regarded as synonymous with $\Delta\chi_m$, the molecular anisotropy.

The usual assumptions of simple molecular orbital theory will be made, namely (*a*) the interaction of the mobile (π-) electrons with the σ-electrons of the localized bonds is negligible; (*b*) the π-electrons themselves may be considered individually so that we deal essentially with a one-electron problem; (*c*) the complete electronic structure is described by allocating the π-electrons, in pairs, to the available one-electron orbitals in ascending order of energy.

There is abundant evidence to suggest that this approximation is satisfactory so long as we consider the ground state only, but the presence of a magnetic field makes it necessary to exercise some care in the choice of formally correct wave functions; these differ from those appropriate without the field in two respects, which we shall now deal with individually.

(i) *Symmetry properties.* Whatever the analytical form of the one-electron wave functions employed, they must all be approximate solutions of the wave equation with the applied field; the mere existence of the field places a considerable restriction on the symmetry properties of such solutions.

The Hamiltonian operator for a single particle is

$$\mathscr{H}(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z) + \frac{1}{2m}\left(\frac{i\hbar e}{c}\,\mathrm{div}\,\mathbf{A} + \frac{2i\hbar e}{c}\,\mathbf{A}.\mathrm{grad} + \frac{e^2}{c^2}|\mathbf{A}|^2\right) \qquad \ldots\ldots(2)$$

where $\mathbf{A}$ is the magnetic vector potential. The existence of a symmetry operation, $x \to x'$, $y \to y'$, $z \to z'$, is described by the invariance of the Hamiltonian under such an operation, i.e. $\mathscr{H}(x',y',z') \equiv \mathscr{H}(x,y,z)$.

Now in the absence of a field the Hamiltonian is invariant under every operation for which $V(x',y',z') \equiv V(x,y,z)$, namely for every operation interchanging like nuclei. But in the presence of a field such operations may no longer be symmetry operations; it is then necessary to examine the field-dependent part of the Hamiltonian. With a uniform field and our choice of axes

$$\left.\begin{aligned} &\mathrm{div}\,\mathbf{A} = 0 \qquad |\mathbf{A}|^2 = \frac{H^2}{4}(x^2+y^2) = \frac{H^2}{4}(r^2 - z^2) \\ &\mathbf{A}.\mathrm{grad} = \frac{H}{2}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{H}{2}\frac{\partial}{\partial\phi}. \end{aligned}\right\} \qquad \ldots\ldots(3)$$

The polar forms of these operators show immediately that the only operation leaving the field-dependent part of the Hamiltonian invariant is an arbitrary rotation about the field direction. Consequently in selecting the appropriate wave functions for a symmetrical molecule by group theory, one can use an n-fold axis normal to the molecule but must exclude all other symmetries. In this connection an important general result holds (Appendix 1): two states which, on account of an n-fold axis, normally exhibit symmetry degeneracy will be separated by the magnetic field and will give equal contributions to the susceptibility in the direction of the symmetry axis.

(ii) *Analytical form.* In all our calculations the field-dependent part of the Hamiltonian will be dealt with as a perturbing term; it is therefore necessary to consider under what conditions the unperturbed wave functions provide a reasonably accurate picture of the behaviour of the electrons in the molecule. Our perturbation calculation will be valid only if the perturbation of an energy level by the field is small compared with the separation of adjacent unperturbed levels. It is easy to see that for very large molecules, approaching in fact the two-dimensional infinite lattice, the method will break down for two reasons.

In the first place the unperturbed energy levels will become infinitely close and as a result of this the situation already pictured is completely changed, the continuum of energy levels being grouped by the perturbation into discrete, degenerate levels corresponding essentially to the quantized states of angular momentum determined *by the field*: in this case the effect of the lattice is simply to determine the mobility of the electrons. Secondly, since the energy levels are extremely close, it is evident that, except at very low temperatures, there will be very considerable excitation of the electrons into higher, unoccupied levels; since both electron mobility and energy level density are strongly dependent on the detailed energy-band structure, especially near the top of a band, a statistical approach is obviously essential. Calculations of this kind have, indeed, been carried through (Peierls 1933, Wilson 1936) and have been successfully applied (e.g. Jones 1934a, b) in a semi-quantitative explanation of the magnetic anisotropy of certain crystals; but it must be emphasized that the mechanism responsible for such anisotropy is essentially distinct from that encountered in dealing with systems of molecular dimensions. For our purposes it is convenient to refer to a system as 'molecular' if the perturbation of its energy levels by the external field is small: in this case we may assume firstly that the broad features of the electronic motion are not appreciably different from those in the unperturbed molecule, and secondly that the system is in the ground state, the large separation of the energy levels effectively precluding excitation. Only for this reason, of course, is it possible to introduce χ by means of (1); strictly, free energies rather than total energies are involved.

As in metal theory there is a choice of two types of wave function on which to base a perturbation calculation. The one generally employed in molecular calculations, the l.c.a.o. approximation (linear combination of atomic orbitals) corresponds to the case of 'tight binding' and in this particular case is almost certainly the more suitable.

It might have been expected that a simple free electron approximation* would at least have served in estimating the order of magnitude of the perturbation but this is not so. A complete calculation (unpublished), based on the free

*'Free' as regards lattice effects, but 'bound' by the finite extent of the lattice.

electron model, shows that only with neglect of all but near-diagonal matrix elements in the second order perturbation energy is diamagnetism ensured; when all elements are rigorously included the diamagnetism may be annulled or even reversed in sign. The explanation of this anomaly seems to lie in the fact that, although the individual matrix elements are small, the total effect, arising from infinite summation, is large. In this particular calculation then, the structure of the energy spectrum at points remote from the occupied level is important, a situation which also arises in metal theory (Wilson 1936, p. 115). Now it is just in these regions that the extreme free electron model will have its greatest shortcomings†, for the energy spectrum is infinite and the density of states increases monotonically with energy. On the other hand, the spectrum of a real lattice (finite or infinite) exhibits a characteristic band structure; in the case of graphite, 'tight binding' (molecular orbital) calculations (Bradburn, Coulson and Rushbrooke 1947, Wallace 1947) lead directly to an energy spectrum which is probably correct in its essentials over the whole of the (half-empty) 2p band. In view of the difficulty of extending the free electron approach in order to get a more realistic picture of the energy spectrum in a finite lattice fragment, it seems that the direct molecular orbital treatment, in the form suggested by London, provides the only practicable type of approach. London's method will be applied, first of all in its original form, the only new difficulties being the extension of the technique to larger systems than hitherto. Later, it is hoped, a more fundamental examination of the whole problem will show how the method may be refined.

§ 3. THE MOLECULAR ORBITAL METHOD

In London's method the molecular orbital (m.o.) of a mobile electron is approximated by linear combination of atomic orbitals (l.c.a.o.) appropriate to the separate atoms *with* the field. From the 'gauge-invariance' of the wave equation (2) it can be shown (Appendix 2) that a suitable atomic orbital for the nth atom is

$$\phi_n(\overline{\mathbf{r}-\mathbf{R}_n}) = \phi_0(\overline{\mathbf{r}-\mathbf{R}_n}) \exp\{-2\pi i\alpha \mathbf{R}_n \cdot \mathbf{A}\} \qquad \ldots\ldots(4)$$

where ϕ_n, ϕ_0 are wave functions for an atom at $\mathbf{R}_n$ and at the origin respectively, $\mathbf{A}$ is the vector potential and $\alpha = (e/hc)$.

With this choice of atomic orbitals, simple m.o. theory gives the energies E of the possible one-electron states as the roots of the secular determinant

$$|(E_0 - E)\delta_{rs} + \beta\epsilon_{rs}\eta_{rs}| = 0 \qquad \ldots\ldots(5)$$

where δ_{rs} is the Krönecker symbol,

$$\left.\begin{aligned} E_0 &= \int \phi_0^*(\overline{\mathbf{r}-\mathbf{R}_s})\mathscr{H}\phi_0(\overline{\mathbf{r}-\mathbf{R}_s})\,d\mathbf{r} \text{ (Coulomb integral)} \\ \beta\epsilon_{rs} &= \epsilon_{rs}\int \phi_0^*(\overline{\mathbf{r}-\mathbf{R}_r})\mathscr{H}\phi_0(\overline{\mathbf{r}-\mathbf{R}_s})\,d\mathbf{r} \text{ (modified resonance integral)} \\ \text{and} \quad \epsilon_{rs} &= \exp\{2\pi i\alpha(\mathbf{R}_r - \mathbf{R}_s)\cdot\bar{\mathbf{r}}\times\mathbf{H}\}. \end{aligned}\right\} \ldots(6)$$

An approximation is involved in withdrawing the exponential factor ϵ_{rs} from integrals involving ϕ_r and ϕ_s, $\mathbf{r}$ being given a mean value $\bar{\mathbf{r}}$, appropriate to the bond r—s. Furthermore, the Coulomb integral is supposed to have the same

† This difficulty is not encountered in the *infinite* lattice problem where, as previously indicated, the calculation is based upon the quantized states of motion about the field direction.

value for each atom and resonance integrals between non-adjacent atoms are neglected by defining

$$\eta_{rs}=1 \quad \text{—atoms r, s, adjacent,}$$
$$\eta_{rs}=0 \quad \text{—atoms r, s, non-adjacent.}$$

It is evident that the usual secular determinant of m.o. theory is modified merely by the presence of the ϵ factors in the off-diagonal elements. This difference, however, generally makes the secular equations much more difficult to solve.

PART II. THE p-POLYPHENYLS

§ 1. INTRODUCTION

The p-polyphenyls may be regarded as the simplest possible examples of a 'graphitic' chain structure, each consisting simply of a number of benzenoid rings linked to each other by one bond only, this being in the para-position (Figure 1). X-ray and electron diffraction evidence suggest that such systems

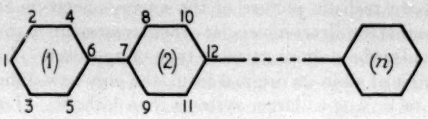
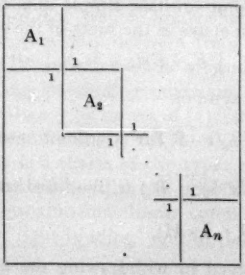


Figure 1.

are very nearly planar (Karle and Brockway 1944) and for the purposes of calculation it will be assumed that this is so; departures arising from a certain amount of steric hindrance could fairly easily be allowed for, but at this stage the main feature of interest is the general effect of conjugation across the connecting links upon the magnetic anisotropy associated with the mobile electrons. The method of calculation has already been outlined in Part I (hereafter referred to as I); the present application is particularly simple and direct.

§ 2. THE MOLECULAR ORBITAL METHOD

Using the numbering system of Figure 1 and putting $x=(E-E_0)/\beta$ the secular determinant for a system of n rings takes the form



.....(1)

where $A_1 \ldots A_n$ are the sixth-order determinants appropriate to the individual rings $1, 2 \ldots n$ and the unit elements arise from the existence of a resonance integral between the last atom of each ring and the first atom of the succeeding ring.

The problem is greatly simplified on using the geometrical interpretation of ϵ_{rs} (I(3)) (London 1937). When the magnetic field **H** is uniform and normal to the plane of the molecule, the exponent becomes simply $2\pi i\alpha HS_{rs}$ where S_{rs} is the area contained by the triangle with vertices at atoms r, s, and the origin, and is reckoned algebraically so that $S_{sr}=-S_{rs}$. Now if a bond r—s is brought into coincidence with a bond r′—s′ by a simple translation, it is not difficult to show that $\epsilon_{r's'}$ is simply related to ϵ_{rs}. In fact

$$\epsilon_{r's'}=\epsilon_{rs}\times\exp\{-2\pi i\alpha H\times(\text{area swept out in the translation of r—s})\}.$$

Choosing the origin at atom 1 and defining $k=\exp\{-\pi i\alpha HS\}$ where S is the area of one ring, it is apparent that

$$A_r=\begin{vmatrix} -x & k^{*r-1}\epsilon_{12} & k^{r-1}\epsilon^*_{12} & & & & \\ k^{r-1}\epsilon^*_{12} & -x & & \epsilon_{24} & & & \\ k^{*r-1}\epsilon_{12} & & -x & & \epsilon^*_{24} & & \\ & \epsilon^*_{24} & & -x & & k^{r-1}\epsilon_{46} & \\ & & \epsilon_{24} & & -x & k^{*r-1}\epsilon^*_{46} & \\ & & & k^{*r-1}\epsilon^*_{46} & k^{r-1}\epsilon_{46} & -x & \end{vmatrix} \quad \ldots\ldots(2)$$

By the following operations (2) may now be reduced to a simpler form:

Multiply the $\{6(r-1)+2\}$th and $\{6(r-1)+4\}$th rows by k^{*r-1},

Multiply the $\{6(r-1)+3\}$th and $\{6(r-1)+5\}$th rows by k^{r-1},

Multiply the $\{6(r-1)+2\}$th and $\{6(r-1)+4\}$th columns by k^{r-1},

Multiply the $\{6(r-1)+3\}$th and $\{6(r-1)+5\}$th columns by k^{*r-1}.

The secular equation then takes on the form

$$\Delta_n=\begin{vmatrix} A_1 & 1 & & & \\ 1 & & & & \\ & A_1 & 1 & & \\ & 1 & & & \\ & & & 1 & \\ & & & 1 & A_1 \end{vmatrix}=0 \quad \ldots\ldots(3)$$

and may be solved by a generalization, due to Coulson and Rushbrooke (1948), of Wolstenholme's well-known treatment of a rather simpler continuant determinant.

With their notation the following second order recurrence relation is found for the Δ_n:

$$\Delta_n-(a-d)\Delta_{n-1}+(bc-ad)\Delta_{n-2}=0. \quad \ldots\ldots(4)$$

Starting from the initial values $\Delta_0=1$, $\Delta_1=\alpha$, it is a relatively simple matter to build up Δ_n and hence obtain the roots directly; in fact this method is very convenient for machine calculation. It is, however, for some purposes more

desirable to use the analytical result given by Coulson and Rushbrooke. In this instance we find

$$\left.\begin{aligned} &\Delta_n = R^n \frac{\sin n\phi}{\sin \phi}[f_1(\phi) - f_2(\phi)] \\ &\text{where } R = 2(x^2-1)(1-\theta^2)^{1/2}, \qquad \cos\phi = \frac{(x^2-1)^2(x^2-5)+4\theta^2}{4(x^2-1)(1-\theta^2)^{1/2}} \\ &f_1(\phi) = \frac{(x^2-1)^2(x^2-4)+4\theta^2}{2(x^2-1)(1-\theta^2)^{1/2}}, \qquad f_2(\phi) = \frac{\sin(n-1)\phi}{\sin n\phi} \end{aligned}\right\} \quad \ldots\ldots(5)$$

and $\theta = \pi\alpha HS$, i.e. a small field-dependent quantity.

Nature of the Roots

We must first consider the case $\theta = 0$. Since no odd powers of x occur it follows immediately that the energy spectrum is symmetrical about $x = 0$. Taking $y = x^2$ it is a simple matter to plot $f_1(\phi)$ and $f_2(\phi)$, for a particular choice of ϕ gives two y values and therefore two branches of $f_1(\phi)$, while $f_2(\phi)$ may be plotted directly. The set of curves for $n = 4$ is shown in Figure 2. There are evidently eight roots, giving sixteen energy levels x ; but from general theory there should be twenty-four values, i.e. twelve roots of $\Delta_n(y) = 0$. It is easily shown that in the special case $\theta = 0$ there is a four-fold degenerate root $y = 1$ owing to the presence of a factor $(y-1)^4$ in $\Delta_4(y)$. In the general case the root $y = 1$ is n-fold degenerate if n is even, while if n is odd there is an additional, $(n+1)$th, root $y = 1$, since one of the intersections of $f_1(\phi)$ and $f_2(\phi)$ is in this case at $\phi = \pi/2$ (i.e. $y = 1$).

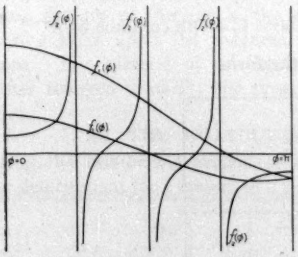


Figure 2.

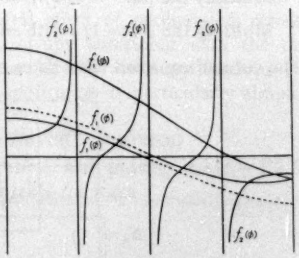


Figure 3.

When $\theta \neq 0$ all the non-degenerate energy levels are slightly modified ; but the whole structure of the ' band ' of n degenerate levels, $y = 1$, is changed, the degeneracy being completely removed. The new situation is shown in Figure 3, again for the case $n = 4$. There are now twelve intersections of $f_1(\phi)$ and $f_2(\phi)$ and since these are all distinct it is evident that degeneracies no longer exist.

§ 3. CALCULATION OF THE SUSCEPTIBILITY

As indicated in I the diamagnetic susceptibility may be calculated by expansion of the perturbed energy levels in powers of H and comparison with the equation $E = E_0 - \frac{1}{2}\chi H^2$. Generally, in terms of x and θ, the relationship takes the form $x = x_0 + x'\theta + x''\theta^2$ and the presence of x' might suggest that certain states give rise to a permanent moment. In fact, states with $x' \neq 0$ are always degenerate and give no observable contribution of this kind (Appendix I).

Summing over the occupied energy levels to find the molecular susceptibility gives $\Sigma x' = 0$ and $\Sigma x'' < 0$, corresponding to a resultant diamagnetism.*

For levels which are initially non-degenerate there is no difficulty ; with $\Delta'(y) = \partial\Delta/\partial y$ it is clear that, since $\Delta = \Delta(y, \theta^2)$ and $\Delta' \neq 0$,

$$y = y_0 - \frac{\Delta(y_0, \theta^2)}{\Delta_0'(y_0)}$$

where y_0 is a root of $\Delta_0(y) = 0$, the suffix 0 indicating $\theta = 0$ (replacing $\Delta_0'(y_0, \theta^2)$ by $\Delta_0'(y_0)$ amounts ultimately to neglecting quantities of order θ^4). Moreover, making a Taylor expansion of $\Delta(y_0, \theta^2)$ about the point $\theta^2 = 0$, and denoting $\partial\Delta/\partial\theta^2$ by $\dot{\Delta}$ we have

$$y = y_0 - \frac{\dot{\Delta}_0(y_0)}{\Delta_0'(y_0)}\theta^2. \qquad \ldots\ldots(6)$$

Now both $\dot{\Delta}$ and Δ' are easily obtained by using the following recurrence relations, which may be derived from (4):

(i) $\Delta_n' = A'\Delta_{n-1} + A\Delta_{n-1}' - B'\Delta_{n-2} - B\Delta_{n-2}'$ $\qquad \ldots\ldots(7)$

where $A = a - d$, $B = bc - ad$ and $\Delta_0 = 1$, $\Delta_1 = a$, $\Delta'_0 = 0$, $\Delta'_1 = a'$.

(ii) $\dot{\Delta}_n = 4\Delta_n + A\dot{\Delta}_{n-1} + 4(\Delta_1 - A)\Delta_{n-2} - B\dot{\Delta}_{n-2}$ $\qquad \ldots\ldots(8)$

with $\dot{\Delta}_1 = 4$, $\dot{\Delta}_2 = 8a$.

These formulae are of a particularly simple form for numerical calculation, A, B, a being given in our case by

$$A = (y-1)^2(y-5), \qquad B = 4(y-1)^2, \qquad a = (y-1)^2(y-4).$$

The n initially degenerate levels must be dealt with separately, for in this case $\Delta_0'(y_0) = 0$. With $y = 1 + \delta$ we must distinguish two cases:

(i) $\delta \sim \theta^2$

From (5) we have, to the second order in θ,

$$\cos\phi = \theta^2/\delta, \qquad f_1(\phi) = 2\theta^2/\delta = 2\cos\phi,$$

and we require the roots of $2\cos\phi = [\sin(n-1)\phi]/\sin n\phi$, $0 < \phi < \pi$, namely $\phi = k\pi/(n+1)$, $k = 1, 2, \ldots . n$.

In the case of n odd, however, the root $\phi = \pi/2$ must be excluded since $\cos\phi = 0$ would imply $\Delta = \pm 2\theta$, contrary to our initial assumptions. For n odd we have already seen there is an $(n+1)$th root $y = 1$, corresponding to $\phi = \pi/2$: this pair of roots will be dealt with next. Bearing in mind this exception we have at $y_0 = 1$

$$y = y_0 + \frac{\theta^2}{\cos\{k\pi/(n+1)\}}, \qquad k = 1, 2, \ldots . n. \qquad \ldots\ldots(9)$$

(ii) $\delta \sim \theta$.

This case only arises when n is odd, as we have already seen. Putting $\phi = \frac{1}{2}\pi + h$, where h is a small quantity, the condition $f_1(\phi) = f_2(\phi)$ gives, to the first order in h, the equation $\delta^2(\delta - 3) + 4\theta^2 = 2(n-1)h\delta$. But from the expression for $\cos\phi$ in terms of δ we have $\delta^2(\delta - 4) + 4\theta^2 = -4\delta h$. Eliminating h we find $(n+1)\delta^3 - 2(2n+1)\delta^2 + 4(n+1)\theta^2 = 0$. We may solve this equation approximately by putting $\delta = a\theta + b\theta^2$, whence

$$a = \pm\left(\frac{2(n+1)}{2n+1}\right)^{1/2}, \qquad b = a^4/8. \qquad \ldots\ldots(10)$$

* Since β is a negative quantity.

We may now profitably summarize our findings. The dependence of any energy level on the field may be found in the form $x = x_0 + x'\theta + x''\theta^2$ which is, of course, derived quite simply from $y = y_0 + y'\theta + y''\theta^2$ since θ is small. We have found that for initially non-degenerate roots $y' = 0$ while y'' is easily calculated from recurrence relations for the degenerate roots, n or $(n-1)$ roots, according as n is even or odd, are separated in pairs with equal and opposite values of y'' (from (9)). As a result there is no net contribution to the diamagnetic susceptibility from a fully occupied group of such energy states. In the case of n odd, however, two of the degenerate roots give equal values of y'' but equal and opposite values of y'. As a result there is a contribution to diamagnetism but no net paramagnetism from an occupied pair of such levels.

The diamagnetic anisotropy $\Delta\chi$ of any molecule of the series is proportional to $\Sigma x''$, the summation being over all occupied energy states. It is a simple matter to evaluate the summed contributions, calculated by the above methods, and to compare the resultant molecular anisotropies with that of the single benzene ring. These calculations have been carried through for $n = 1, 2, \ldots 6$; the results are illustrated in Figure 4.

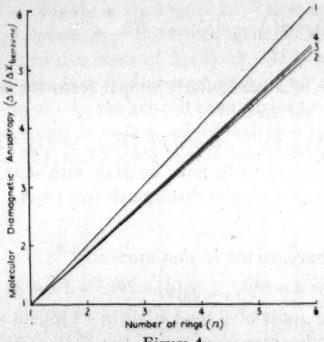


Figure 4.

1. Rings independent (conjugation neglected).
2. Effect of conjugation. Pauling's method.
3. ,, ,, ,, London's method.
4. ,, ,, ,, London's method with overlap correction.

For diphenyl ($n = 2$) $\Delta\chi/\Delta\chi_{\text{benzene}} = 1{\cdot}869_5$. For $n > 2$ the relationship very quickly becomes almost perfectly linear and may be written in good approximation

$$\Delta\chi/\Delta\chi_{\text{benzene}} = 0{\cdot}859n + 0{\cdot}153. \qquad \ldots\ldots(11)$$

The Effect of Overlap

It is not difficult to refine these calculations somewhat by taking into account the substantial non-orthogonality of orbitals on adjacent atoms. The method first used by Wheland (1941) has been employed for this purpose by Brooks (1941).

As will be seen from Figure 4, the effect of correction for overlap is remarkably small; indeed, even for an overlap integral $\delta = 0{\cdot}25$ the effect is almost negligible. For diphenyl we find $\Delta\chi/\Delta\chi_{\text{benzene}} = 1{\cdot}876_5$ while for $n > 2$ the approximate formula becomes

$$\Delta\chi/\Delta\chi_{\text{benzene}} = 0{\cdot}865n + 0{\cdot}148. \qquad \ldots\ldots(12)$$

§ 4. APPLICATION TO VERY LONG CHAINS

Although the present theory cannot be applied to an infinite system for reasons discussed in I, it is possible to deal with chains of such a length that, while the perturbation calculation is still valid, the approximate solution is obtained by a limiting process in which $n\to\infty$. The circumstances in which the solution is valid follow from the analysis.

It is possible to make use of the fact that in the limit $n\to\infty$ the energy levels occur for equi-spaced ϕ values. Provided θ^2 remains sufficiently small (vanishing more rapidly, in fact, than $1/n$) $\Delta\sim\theta^2$, and we may put $y=y_0+\Delta$, obtaining from (5) to the first order in Δ

$$\Delta\{4\cos\phi-(y_0-1)(3y_0-11)\}=\theta^2\{4+2(y_0-1)\cos\phi\}$$

from which Δ, and hence y'' and x'', are easily found for any energy value. In this case, however, the energy levels fall into two contiguous bands, extending from $x_0=\sqrt{2}-1$ to $x_0=\sqrt{3}$ (Band I) and from $x_0=\sqrt{3}$ to $x_0=\sqrt{2}+1$ (Band II), the former containing the ' degenerate band ' of n levels at $x_0=1$: it is then possible to evaluate the summed contributions $\Sigma x''$ by integration over each energy band. From a previous section it is obvious that as $n\to\infty$ the degenerate band gives a vanishing contribution. In each band the energy level density in ϕ is n/π while y_0 is easily found to be $y_0=3-2\sqrt{2}\cos\phi/2$ (Band I) or $y_0=3+2\sqrt{2}\cos\phi/2$ (Band II). It follows finally on putting $\sqrt{2}\cos\phi/2=z$ that

$$\Sigma x''\to\frac{n}{4\pi}\int_0^{\pi}\frac{z^2-z-1}{(z-1)(3-2z)^{1/2}}\,d\phi. \qquad \text{(Band I)} \quad \ldots\ldots(13)$$

$$\Sigma x''\to-\frac{n}{4\pi}\int_0^{\pi}\frac{z^2+z-1}{(z+1)(3+2z)^{1/2}}\,d\phi. \qquad \text{(Band II)} \quad \ldots\ldots(14)$$

A singularity occurs at $\phi=\pi/2$ ($x_0=1$) in the integrand of (13), which must therefore be split, developed in series about this point, and evaluated by a limiting process; there is no net contribution to $\Sigma x''$ from those levels in the vicinity of this point.

These integrals, and the slightly more complicated ones arising when overlap is taken into consideration, are easily evaluated numerically giving the limiting results

$$\left.\begin{aligned}\Delta\chi/\Delta\chi_{\text{benzene}}&=0{\cdot}84_8 \quad (\text{overlap } \delta=0)\\ \Delta\chi/\Delta\chi_{\text{benzene}}&=0{\cdot}85_7 \quad (\text{overlap } \delta=0{\cdot}25)\end{aligned}\right\} \quad \ldots\ldots(15)$$

It is pleasing to find that the linearity of the relationship is so well preserved: whether this limiting result is of any value depends, of course, on the range of n for which the calculation is valid.

Range of Validity of Results

The simplest criterion for validity of the perturbation calculation is that the ratio $\delta/\Delta\ll 1$, δ being the perturbation of a level and Δ the separation of adjacent levels. It is not difficult to show that δ/Δ has its greatest value in and around the degenerate band and at the bottom of Band I. In fact, the maximum value of this ratio is $\delta/\Delta=\sqrt{2}(4n/\pi)^2\theta^2$. Remembering $\theta=\pi(e/hc)HS$, and taking $S\sim 5\times10^{-16}$ cm^2, $H=10^4$ gauss, it appears finally that the calculations of this paper should be valid for chains of up to at least 2,000 rings; not until well above this limit is it necessary to regard the system as a one-dimensional crystal. This upper limit is perhaps surprisingly high but in this respect the system under

consideration is rather unique; for nearly all other types of molecule, increase in size is accompanied by a rapid increase in the effect of the field, which invalidates the calculations at a much lower size limit. It follows, therefore, that (15) may be regarded as significant.

§ 5. CONCLUSION

From a theoretical point of view the results obtained may be regarded as very satisfactory: in particular, the view that properties of the whole π-electron gas should not be very strongly dependent on the precise choice of wave functions is supported by the fact that our results are very insensitive to variations in overlap integral. It is probably for this same reason that Pauling's semi-classical model (1936) is so successful. Indeed, a contradiction between the predicted variations of $\Delta\chi$ with chain length, using the present method and Pauling's method, would not be expected in view of the general agreement of the two theories for many other molecules (London 1937). It is gratifying to find that the discrepancy actually pointed out by London in the case of diphenyl is due simply to a numerical error (McWeeny 1949). The results of our calculations do in fact show (Figure 4) that there is no serious divergence between the predictions of the two theories.

For comparison purposes Figure 4 includes a curve showing the variation in $\Delta\chi$ assuming the n individual rings to be independent, the contributions of the rings then being simply additive. Clearly the effect of conjugation across the connecting links is to decrease the mean anisotropy per free electron by about 15%. At first sight this result is unexpected, since conjugation leads to a greater delocalization of the electrons. Pauling's picture provides the simplest interpretation of this effect, for the linkage of single rings to form a polyphenyl chain results in a reduction of the mean electron density per bond, and hence the ring currents, which give rise to the induced magnetic moment, are feebler. We might expect this effect to be a quite general characteristic of one-point linkages. On the other hand if a number of rings are linked to each other by more than one bond, further rings will be formed incidentally and the effect of diminishing electron density is likely to be greatly outweighed by that due to the increased number of induced ring currents. Indeed our results seem to provide some confirmation of Pauling's view that the mean electron density per bond is a significant factor in determining the π-electron susceptibility, a view which is difficult to maintain on closer examination of the semi-classical model and was, indeed, rejected by London. Reasons for the success of Pauling's method, which though plausible is fundamentally unsound, will be discussed later.

At present the experimental data available (Lonsdale 1937) are too limited to admit a detailed comparison with these conclusions. In particular, there is a very great uncertainty in $\Delta\chi$ for the benzene molecule and the writer is not aware of any experimental results at all for n greater than 4. One remark might be made regarding the applicability of our results to actual molecules, for the structures considered in this paper are hypothetical in the sense that they possess a common ring size and a common resonance integral. In fact, in going along the series from one molecule to the next there is a small change of mean bond order and consequently of ring size and resonance integral. At this stage it appears neither justifiable nor, indeed, feasible, with crude m.o. theory, to take in to account second order effects of this kind. It may be worth noting, however, that, with

this theory, the admitted variations in S and β would produce oppositely directed changes in $\Delta\chi$ and hence, since the variations are in any case small, would probably give an insignificant residual effect. The calculations of this paper may, therefore, confidently be expected to apply to actual molecules (within the limitations of crude m.o. theory), possibly with slight modifications for molecules up to, say, triphenyl, beyond which variations in mean bond order are extremely small. It would, then, seem very desirable that a thorough comparison between theory and experiment should be made; indeed, the present series of molecules appears to offer a very convenient testing ground for the whole theory.

APPENDIX I

The following result will be proved: when a molecule possesses an n-fold axis of symmetry, $n>2$, the available one-electron energy levels are degenerate in pairs in the absence of the field: the states represented by such a pair give equal contributions to the diamagnetic susceptibility along the symmetry axis but correspond to states of equal and opposite permanent moment. It follows that by choosing new combinations of the degenerate states these could be regarded as giving no effective permanent moment but simply equal contributions to the diamagnetic susceptibility.

When accidental degeneracies occur no general conclusions can be formed as regards the diamagnetic susceptibilities of the various states. It is easily seen, however, that any state of given permanent moment is accompanied by one of equal and opposite moment, for two such states must correspond to eigenvalues $\pm m_z$ of the operator $\mathbf{M}_z$. Again, therefore, there is no real effect since two combinations of zero mean moment can be formed. These remarks are illustrated in II, while the theorem above will be useful in dealing with symmetrical systems (e.g. coronene) since the susceptibility of only one of each degenerate pair of states need now be calculated.

Consider then a molecule possessing an n-fold axis, with which we associate the group C_n. It is well known that all possible irreducible representations of C_n in the complex field are uni-dimensional and also that the solutions of the Schrödinger equation constitute a basis for a representation of the symmetry group of the system. It follows that under an operation s of the group C_n a function ψ_n, of that basis which is adapted to a decomposition of the representation into a direct sum of uni-dimensional representations, must be transformed according to $\psi_n \rightarrow \psi_n' = D_n(s)\psi_n$ where $D_n(s)$ is a representative (the nth, say) of the group element s. In the uni-dimensional case, of course, $D_n(s) = \chi_n(s)$ where $\chi_n(s)$ is the character of the nth representative of s.

Now the character systems of the n non-equivalent irreducible representations of C_n occur in conjugate pairs, except for either one or two real characters which exist according as n is odd or even. As we shall see, degeneracy is associated with the existence of 'conjugate representations'; it is at once apparent, then, that the theorem will apply only when at least one pair of conjugate representations exists, i.e. with n greater than 2. Let ψ_1, ψ_2 be functions providing bases for representations $D_1(s)$, $D_2(s)$ of s and suppose the representations are conjugate. Then under the operation s

$$\psi_1 \rightarrow \psi_1' = D_1(s)\psi_1, \qquad \psi_2 \rightarrow \psi_2' = D_1^*(s)\psi_2.$$

Now ψ_1, ψ_2 are solutions of the Schrödinger equation $\mathscr{H}\psi = E\psi$ and from above it is clear that ψ_1, ψ_2 are generally complex. But only ψ_1^* (or multiples) has the transformation properties ascribed to ψ_2; we need only enquire then whether the eigenfunctions ψ_1, ψ_1^* correspond to the same eigenvalue, E_1, say. Now $\mathscr{H} = \mathscr{H}_0 + iAH + BH^2$ where $\mathscr{H}_0$ is the (real) Hamiltonian operator in the absence of the field H. Two cases arise:

(*a*) *Field absent* ($\mathscr{H}^* = \mathscr{H}$). Since $\mathscr{H}\psi_1 = E_1\psi_1$, $\mathscr{H}^*\psi_1^* = E_1\psi_1^*$, i.e. since $\psi_1^* = \psi_2$ and $\mathscr{H}^* = \mathscr{H}$, it follows that $\mathscr{H}\psi_2 = E_1\psi_2$ so that ψ_1 and ψ_2 are eigenfunctions belonging to the same eigenvalue E_1 (and are distinct since ψ_1 is complex). By taking sum and difference it follows also that there are two linearly independent *real* eigenfunctions.

(*b*) *Field present* ($\mathscr{H}^* \neq \mathscr{H}$). In this case, letting $\mathscr{H}\psi_2 = E_2\psi_2$ it follows that $\mathscr{H}\psi_1^* = E_2\psi_1^*$. Consequently $\mathscr{H}^*\psi_1 = E_2\psi_1$, but by definition $\mathscr{H}\psi_1 = E_1\psi_1$. Now $\mathscr{H}^*$ is the same operator as $\mathscr{H}$ except for a sign reversal in the term of odd degree in H; if then

$$\mathscr{H}\psi_1 = (E_0 + \lambda H + \mu H^2 + \ \ldots)\psi_1,$$

it follows that

$$\mathscr{H}^*\psi_1 = (E_0 - \lambda H + \mu H^2 - \ \ldots)\psi_1,$$

i.e. whereas

$$E_1 = E_0 + \lambda H + \mu H^2 + \ \ldots$$

we find

$$E_2 = E_0 - \lambda H + \mu H^2 - \ \ldots$$

The energy state E_0 is therefore split by the field into two distinct states. Moreover since λ and μ are respectively proportional to the permanent moment and diamagnetic susceptibility of a state the theorem follows at once.

APPENDIX II

The one-electron solutions of the single-atom Schrödinger equation, i.e. the atomic orbitals, are dependent on the particular choice of zero point of the vector potential, although of course $|\psi|^2$ must be invariant to this choice. This is the property of 'gauge invariance' and arises from the arbitrary nature of the electromagnetic potentials. We shall simply indicate here how the appropriate form of the atomic orbitals follows from this property.

The magnetic vector potential $\mathbf{A}$ is arbitrary to the extent of an additive irrotational vector field. Taking the magnetic field direction as z axis the simplest choice of $\mathbf{A}$ is

$$\mathbf{A} = \tfrac{1}{2}\mathbf{H} \times \mathbf{r} = -\tfrac{1}{2}Hy\mathbf{i} + \tfrac{1}{2}Hx\mathbf{j},$$

$\mathbf{A}$ then being zero at the origin of coordinates.

Let ψ be a solution of the wave equation with the magnetic field: then the gauge invariance of the equation is expressed by (cf. Wilson 1936)

$$\mathbf{A} \rightarrow \mathbf{A} + \text{grad}\, U, \qquad \psi \rightarrow \psi \exp\{-2\pi i\alpha U\}, \qquad \alpha = e/hc.$$

Now consider a translation of axes in the (x, y) plane, the new origin O′ now being the point $(-X, -Y)$ and define the vector potential appropriate to the new origin as $\mathbf{A}' = -\tfrac{1}{2}Hy'\mathbf{i} - \tfrac{1}{2}Hx'\mathbf{j}$ i.e. $\mathbf{A}' = \mathbf{A} + (-\tfrac{1}{2}HY\mathbf{i} + \tfrac{1}{2}HX\mathbf{j})$. Then this constitutes a gauge transformation if $-\tfrac{1}{2}HY\mathbf{i} + \tfrac{1}{2}HX\mathbf{j} = \text{grad}\, U$. An obvious and sufficient solution is

$$U = -\tfrac{1}{2}HYx + \tfrac{1}{2}HXy = \tfrac{1}{2}\mathbf{R}.\mathbf{r} \times \mathbf{H} = \mathbf{R}.\mathbf{A}$$

where **R** is the position vector of the old origin in the new frame. This result shows simply that if a new origin of the vector potential is chosen, whose position vector in the original frame is $-\mathbf{R}$, then the original wave function ψ is multiplied by a phase factor $\exp\{-2\pi i\alpha\mathbf{R}.\mathbf{A}\}$. The atomic orbitals employed in constructing an l.c.a.o. molecular orbital are thus identical for similar atoms, except for a phase factor depending on the position vectors ($\mathbf{R}_n$) of the various atoms relative to a common origin, chosen for convenience in dealing with the molecule as a whole.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my indebtedness to Professor C. A. Coulson for providing me with approximate numerical values of the p-polyphenyl energy levels. I also wish to record my thanks to my wife for carrying through many of the calculations outlined in §3 of Part II.

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A Quantum Mechanical Treatment of the Lithium Fluoride Crystal

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ABSTRACT. A simplified quantum-mechanical model for the LiF crystal is described. The lattice parameter, cohesive energy and compressibility are calculated using three different choices of wave function for the fluorine ion in the crystal; these are (i) the Hartree wave functions for the free ion F^-, (ii) wave functions orthogonalized to the 1s-orbitals of the six nearest neighbour lithium ions, (iii) functions similar to (ii) but based on wave functions for the free ion which have been contracted to give agreement with the diamagnetism of F^-.

The results obtained in (i) are in fair agreement with the empirical values. Large discrepancies are observed when the more complete wave functions (ii) are employed. This is taken as indicating that the Hartree wave functions for the free ion are too diffuse and the results of the third calculation, which agree well with experiment, substantiate this interpretation.

§ 1. INTRODUCTION

Modern theories of ionic crystals may be divided roughly into two main types, classical treatments and those based on quantum mechanics. The classical theory of ionic crystals, which has been developed to a great extent by Born and Mayer (1932), leads to a semi-empirical expression for the cohesive energy, containing two parameters which are adjusted to give agreement with experimentally determined data on the lattice spacing and compressibility. In this way, a fairly satisfactory model expressing many of the properties of ionic crystals can be built up, but the relation of these expressions to the electronic wave functions of the ions composing the crystal is left open. A more fundamental quantum-mechanical approach has been adopted by Hylleraas (1930), Landshoff (1936, 1937) and more recently by Löwdin (1948), who has made elaborate calculations for a number of ionic crystals. The physical significance of some of the factors involved in these treatments is not quite clear and the present paper attempts to give a simpler description, whose meaning may be more easily followed, for the case of lithium fluoride.

§ 2. DESCRIPTION OF THE MODEL

In the following work it is assumed that the metal and halogen ions are arranged in the usual cubic lattice array and that the structure is completely ionic. Purely central forces act between ions, and the force between two ions which are not nearest neighbours is considered to be the ordinary electrostatic term. Only uniform lattice deformations are allowed and the energy associated with the thermal vibration of the ions is not considered.

The substance lithium fluoride was chosen for two reasons. In the first place, the calculations are simplified by keeping the metal ion fairly small compared with the halogen ion; thus in our model the lithium ion is treated as a unit positive

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point charge and account of the 1s-electrons is taken only indirectly in the orthogonalization relations. Secondly, it has been pointed out (Sherman 1932, Verwey and de Boer 1936, 1940) that repulsion between the closed shells of the halogen ions is probably significant in most lithium halides. An examination of the ratios of the radii of the various halogen ions to that of the lithium ion indicates that only in the case of fluorine is there some justification for neglecting this effect.

On the basis of this model, the total energy of the crystal $U(\rho)$ per ion pair, stated relative to the free ions, is given by

$$U(\rho) = -\alpha_M/\rho + 6/\rho + 6w(\rho) \qquad \ldots\ldots(1)$$

where ρ is the nearest neighbour distance in the lattice and $w(\rho)$ represents the average interaction energy between a fluorine ion and one of its nearest neighbour lithium ions. The Madelung constant α_M has the value 1·7476 for the cubic structure. In equation (1) and all subsequent work, unless otherwise stated, atomic units * are employed. The term $6/\rho$ is introduced to cancel the nearest neighbour contribution in the Madelung sum. In essence the problem is reduced to the evaluation of $w(\rho)$ and several attempts to do this are outlined in the next section.

§ 3. CALCULATION OF $w(\rho)$

In calculating the energy of interaction of a fluorine ion with its nearest neighbours, the structure of the outer parts of the fluorine ion is of primary importance. To achieve simplification, all details of the inner structure were discarded and the fluorine ion was treated as a nucleus of charge +5, surrounded by a shell of six 2p-electrons.

For a free fluorine ion at position ' a ', these outer electrons are described in the one-electron approximation by assigning a pair of electrons of opposite spin to each of the three orbitals given by the equations

$$\left.\begin{aligned} \psi_x &= K_1 R(r_a) \sin\theta_a \sin\phi_a, \\ \psi_y &= K_1 R(r_a) \sin\theta_a \cos\phi_a, \\ \psi_z &= K_1 R(r_a) \cos\theta_a, \end{aligned}\right\} \qquad \ldots\ldots(2)$$

where r_a, θ_a and ϕ_a are the usual polar coordinates of an electron relative to the nucleus at position ' a '. $R(r_a)$ is the radial portion of the wave function and was chosen to satisfy

$$\int_0^\infty [r_a R(r_a)]^2 \, dr_a = 1. \qquad \ldots\ldots(3)$$

For normalization of the wave functions

$$K_1 = (3/4\pi)^{1/2}. \qquad \ldots\ldots(4)$$

Hartree (1935) has used the method of the self-consistent field without exchange to calculate the radial density distribution of the 2p-electrons of a free fluorine ion. This function was suitably normalized and fitted with an analytic expression of the form

$$r_a R(r_a) = r_a^2 \{A_1 \exp(-\alpha_1 r_a) + A_2 \exp(-\alpha_2 r_a)\} \qquad \ldots\ldots(5)$$

* The atomic unit of length is a_H, the radius of the first Bohr orbit of the hydrogen atom : 1 A.U. of length $= 0{\cdot}5292 \times 10^{-8}$ cm. The atomic unit of energy is e^2/a_H, where e is the electron charge : 1 A.U. of energy = 27·205 ev.

The constants A_1, A_2, α_1, α_2 were chosen to satisfy (3), to keep the maximum of the distribution approximately unaltered and to fit the outer part of the distribution from $r_a=2$ to $r_a=6$, the equilibrium interatomic distance in lithium fluoride being 3·8 A.U. The values obtained for the four constants were:

$$A_1=7{\cdot}2340,\ \alpha_1=2{\cdot}37;\ A_2=0{\cdot}3100,\ \alpha_2=0{\cdot}85. \qquad \ldots\ldots(6)$$

(i) *Simple Perturbation Calculation*

The problem of the interaction of a fluorine ion in a crystal with a neighbouring lithium ion at 'b' (Figure 1), a distance ρ along the x-axis, was treated first by

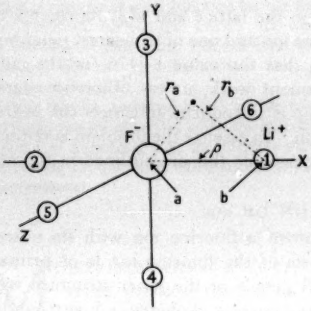

Figure 1.

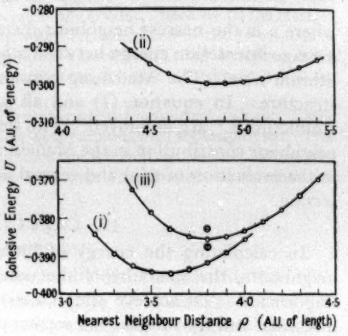

Figure 2. (i) Simple perturbation calculation, (ii) wave functions orthogonalized, (iii) wave functions adjusted to fit diamagnetism. Position of equilibrium according to classical theory and calculated by
⊖ Mayer and Helmholtz (1932).
⊕ Verwey and de Boer (1936).

taking the potential energy of the metal ion

$$v=-1/r_b \qquad \ldots\ldots(7)$$

as a perturbation of the Hamiltonian for the single electron wave functions given by (2). As indicated in Figure 1, r_b is the radial distance of the electron from the position 'b' of the lithium ion. Then

$$w(\rho)=5/\rho+\Delta v(\rho), \qquad \ldots\ldots(8)$$

where

$$\Delta v(\rho)=2[(\psi_x|v|\psi_x)+(\psi_y|v|\psi_y)+(\psi_z|v|\psi_z)] \qquad \ldots\ldots(9)$$

and the usual matrix notation

$$(\psi_x|v|\psi_x)=\int \psi_x^* v\psi_x\, d\tau \qquad \ldots\ldots(10)$$

has been used. The wave functions defined by equations (2) to (6) were substituted in (9) and the integrals evaluated. Thus

$$\Delta v(\rho)=-2K_1^2[A_1^2J_5(2\alpha_1,0,\rho)+2A_1A_2J_5(\alpha_1+\alpha_2,0,\rho)+A_2^2J_5(2\alpha_2,0,\rho)] \qquad \ldots\ldots(11)$$

where the $J_n(\alpha,\beta,\rho)$ are two-centre integrals, expressions for which have been given by Coulson (1942).

Finally, the total energy was calculated numerically from the formula

$$U(\rho) = (36 - \alpha_M)/\rho + 6\Delta v(\rho). \qquad \ldots\ldots (12)$$

The results plotted as a function of ρ are shown in curve (i) of Figure 2. A suitable analytic expression, such as a second degree polynomial, was fitted to the portion of the curve around the minimum and the equilibrium position determined by differentiation. The lattice parameter, cohesive energy and compressibility corresponding to equilibrium are indicated in the first row of the Table and can be compared with the empirical values given in the fourth row. The agreement obtained is fair, but it is clearly rather a drastic approximation to use orbitals appropriate to the free ion in the interior of the crystal. An essential refinement is introduced in the next sub-section.

Summary of Results

Description	Lattice parameter A	Cohesive energy (k cal/mol.)	Compressibility (10^{-12} cm^2/dyne)
(i) Simple perturbation calculation	3·78	−247·4	1·8
(ii) Wave functions orthogonalized	5·16	−188·1	4·8
(iii) Wave functions adjusted to fit diamagnetism	4·02	−242·0	1·7
Empirical values *	4·02	−240·1 (M. & H.) −243·0 (V. & de B.)	1·53 at 303° K. 1·4 at 0° K.
Theoretical results of Löwdin (1948)	4·79	−199·5	4·0

* The value of the lattice parameter is that measured at 273° K.; the value at 0° K. would be approximately 1% less (Verwey and de Boer 1940). Since an experimental value of the electron affinity of fluorine is not available the cohesive energies quoted are those calculated according to the classical theory by Mayer and Helmholtz (1932) and Verwey and de Boer (1936) respectively. The compressibility was measured by Slater (1924) at 303° K. and the value at 0° K. obtained by linear extrapolation.

(ii) *Calculation using Orthogonalized Orbitals*

Coulson and Duncanson (1942) in their discussion of the lithium molecule have indicated the need to assign the individual electrons to mutually orthogonal orbitals, and in particular to orthogonalize the outer orbitals on one atom to the inner orbitals on its neighbour. Löwdin (1950) has given an elegant and rigorous treatment of this question. The idea of orthogonalized orbitals was applied, in a greatly simplified form, to the present problem.

The orbitals for the six outer electrons of the fluorine ion within the crystal were taken to be

$$\left.\begin{aligned} \psi_x' &= C(\psi_x - S\phi_1 + S\phi_2), \\ \psi_y' &= C(\psi_y - S\phi_3 + S\phi_4), \\ \psi_z' &= C(\psi_z - S\phi_5 + S\phi_6), \end{aligned}\right\} \qquad \ldots\ldots (13)$$

where

$$\phi = K_2 \exp(-\beta r_b) \qquad \ldots\ldots (14)$$

represents a 1s-orbital for a lithium ion at position 'b' and the subscripts 1 to 6 attached to ϕ indicate that 'b' is one of the points $(\rho, 0, 0)$, $(-\rho, 0, 0)$, $(0, \rho, 0)$, $(0, -\rho, 0)$, $(0, 0, \rho)$, $(0, 0, -\rho)$ respectively (see Figure 1). A similar meaning is

implied when subscripts are attached to v previously defined by equation (7). The value $\beta = 2{\cdot}69$ was used (Hylleraas 1930, Duncanson and Coulson 1944), and for normalization

$$K_2 = (\beta^3/\pi)^{1/2}. \qquad \ldots\ldots(15)$$

The overlap integral S is given by

$$S = \int \psi_x \phi_1 \, d\tau = -\int \psi_x \phi_2 \, d\tau = \ldots\ldots \text{etc.} \ldots\ldots = -\int \psi_z \phi_6 \, d\tau, \qquad \ldots\ldots(16)$$

while

$$C = (1 - 2S^2)^{-1/2}. \qquad \ldots\ldots(17)$$

The orbitals defined by equations (13) to (17) are mutually orthogonal and very nearly orthogonal to the 1s-orbitals of the six nearest neighbour lithium ions.

The single electron Hamiltonian operator for an outer electron of the free fluorine ion is

$$H = -\tfrac{1}{2}\nabla^2 + V(r_a). \qquad \ldots\ldots(18)$$

$V(r_a)$ is the appropriate average potential function given by the self-consistent field method. The wave functions (2) satisfy

$$H\psi = \epsilon\psi \qquad \ldots\ldots(19)$$

where ϵ differs from the energy parameter defined by Hartree (1928) by a factor $-\frac{1}{2}$. The potential function $V(r_a)$ was expressed in analytic form by working backwards from the radial distribution using

$$V(r_a) = \epsilon - \frac{1}{r_a^2} + \frac{1}{2r_a R(r_a)} \frac{d^2}{dr_a^2}[r_a R(r_a)]. \qquad \ldots\ldots(20)$$

Combining this with equation (5) gave

$$V(r_a) = \epsilon + f(r_a) \qquad \ldots\ldots(21)$$

in which

$$f(r_a) = \frac{\alpha_1(\alpha_1 r_a - 4)\exp\{-(\alpha_1 - \alpha_2)r_a\} + A_2\alpha_2(\alpha_2 r_a - 4)/A_1}{2r_a(\exp\{-(\alpha_1 - \alpha_2)r_a\} + A_2/A_1)}. \qquad \ldots\ldots(22)$$

Assuming the single electron Hamiltonian applicable in the crystal to be

$$H' = H + \sum_{i=1}^{6} V_i, \qquad \ldots\ldots(23)$$

the interaction energy was expressed as

$$w(\rho) = 5/\rho + (\psi_z' | H' | \psi_z') - (\psi_z | H | \psi_z). \qquad \ldots\ldots(24)$$

In working out the matrix elements in equation (24), all integrals involving three centres or two centres farther apart than the nearest neighbour distance ρ were neglected; then

$$w(\rho) = 5/\rho + C^2[\Delta v(\rho) + 2S\{S(\tfrac{1}{2}\beta^2 - \beta + (\phi_5 | V(r_a) | \phi_5) - \epsilon) - 2(\phi_5 | v_5 | \psi_z)\}] \quad \ldots(25)$$

As an approximation $(\phi_5 | V(r_a) | \phi_5)$ was replaced by $V(\rho)$, the value of V at a nearest neighbour lithium ion; it then follows that

$$U(\rho) = (36 - \alpha_M)/\rho + 6C^2[\Delta v(\rho) + 2S\{S(\tfrac{1}{2}\beta^2 - \beta + f(\rho) - 2(\phi_5 | v_5 | \psi_z)\}]. \qquad \ldots\ldots(26)$$

This formula becomes identical with (12) if the overlap integral is very small and can be neglected.

The matrix elements $(\phi_5 | v_5 | \psi_z)$ and S can be expressed in terms of Coulson's J-integrals and numerical values determined. Curve (ii) of Figure 2 was plotted from equation (26) and the values of the lattice parameter, cohesive energy and

compressibility are indicated in the second row of the Table. These results show large deviations from the empirical values and are comparable with the more exact calculations of Löwdin (1948). For reference the latter data are given in the last row of the table.

Löwdin has suggested that the inclusion of $F^- - F^-$ interactions would result in better theoretical values. On the other hand one might expect this interaction to be repulsive and that it would increase the lattice spacing rather than decrease it. The present authors considered that more reasonable sources of these discrepancies might be the over-diffuseness of the Hartree wave functions employed, or a partial covalent character of the binding.

(iii) *Use of Wave Functions adjusted by use of the Diamagnetic Susceptibility of the Fluorine Ion*

It is well known that the Hartree simple product wave function neglects the exchange correlation of the electron motions, arising from the antisymmetry of the wave function. In general, the wave function calculated without exchange is too extended and antisymmetrization leads to a contraction. The diamagnetic susceptibility provides a means of studying this question. Using the wave functions defined by equations (2) to (6), the diamagnetic susceptibility of the free fluorine ion was calculated from the formula (Van Vleck 1932, p. 206)

$$\chi_{\text{mol}} = -2{\cdot}832 \times 10^{10} \Sigma \overline{r^2}. \qquad \ldots\ldots(27)$$

In this relation χ_{mol} is the diamagnetic susceptibility per gram mol. and r is measured in centimetres. Only contributions of the 2p-electrons to the sum $\Sigma \overline{r^2}$ were considered to be significant. The value $\chi_{\text{mol}} = -15{\cdot}6 \times 10^{-6}$ resulting from this calculation, when compared with $-8{\cdot}1 \times 10^{-6}$ given by Pauling (1927) indicates that the wave function is too diffuse.

Instead of recalculating the self-consistent field including exchange, it was decided to attempt a more empirical readjustment of the wave function. The radial distribution given by (5) and (6) was contracted by introduction of a linear scale factor and then renormalized. The scale factor was chosen to yield a diamagnetic susceptibility of $-8{\cdot}1 \times 10^{-6}$ in a calculation of the type outlined above. The new values of the constants obtained by this drastic procedure were

$$A_1 = 16{\cdot}4459,\ \alpha_1 = 3{\cdot}29;\quad A_2 = 0{\cdot}70387,\ \alpha_2 = 1{\cdot}18. \qquad \ldots\ldots(28)$$

Evaluation of the interaction energy given by equation (26) was repeated using these new constants. The result is indicated graphically in curve (iii) of Figure 2 and the lattice parameter, cohesive energy and compressibility are shown in the third row of the table. Considering the approximations involved, the agreement with the accepted values is very good, and must depend to some extent on a cancellation of the various factors omitted.

(iv) *Covalency*

The results of the previous sub-section indicate that covalent binding is probably not very significant in determining the energy of a uniformly dilating LiF lattice. Inclusion of covalency might help to reduce the compressibility, as might also the inclusion of anion–anion interaction.

A rough calculation of the covalency in a diatomic LiF molecule was made. The exchange energy integral between the lithium 2s- and fluorine 2p-orbitals

was of the order of 1·6 ev. while the energy threshold observed for ultra-violet absorption in the crystal is about 12 ev. On this basis it does not seem likely that the charge distribution will differ much from the purely ionic state in the crystal.

§ 4. CONCLUSION

In the previous sections a model for LiF has been described, by means of which the lattice parameter, cohesive energy and compressibility of the crystal may be estimated from the Hartree wave functions for F^- adjusted to fit the diamagnetism. It is of interest to examine briefly the law of interaction between nearest neighbours obtained in this calculation.

Over the range from $\rho=3{\cdot}4$ to $\rho=4{\cdot}4$ the energy of interaction between nearest neighbours as calculated in sub-section (iii) can be represented to a few hundredths of one per cent by the empirical relation

$$w(\rho)=-1/\rho+ce^{-\rho/\gamma}, \qquad \ldots\ldots(29)$$

with $c=6{\cdot}4786$ and $\gamma=0{\cdot}6065$. This may be interpreted as an electrostatic attraction combined with an exponential repulsion similar to that used by Born and Mayer (1932). From a study of 20 alkali halides the latter authors obtained a value of $\gamma=0{\cdot}345\times10^{-8}$ cm. $=0{\cdot}652$ A.U. An inverse power law $D\rho^{-n}$ was not as suitable as the exponential form for representing the repulsive interaction. The value of $n\simeq6{\cdot}44$ gave the best fit to the data. Slater (1924) has derived a value of $n=5{\cdot}9$ from his compressibility results.

In conclusion, it should be noted that formula (25) for $w(\rho)$ has been calculated on the basis of interaction with six neighbours and differs from the result obtained when only one neighbour is considered. Furthermore, only uniform distortions of the lattice have been treated. Extension of the calculations to include polarization of the ions in asymmetrical fields, surface effects, etc., would be of interest. In such circumstances covalency may be of increased importance.

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Epitaxial Crystal Growth of Silver on Rock-Salt (110) and (111) Faces

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ABSTRACT. It has long been known that silver can grow epitaxially on a rock-salt cleavage face. It has now been found by electron diffraction that silver also grows in parallel orientation on (110) and (111) faces of rock-salt and that the silver crystals are twinned repeatedly on their {111} faces. A new example of rotational slip has been noted in which silver crystals were found to have slipped rotationally on their {110} planes.

§1. INTRODUCTION

Many workers (see Goche and Wilman 1939) have studied the structure and orientation of silver films condensed *in vacuo* on rock-salt cleavage faces. On a heated cube-face of rock-salt silver usually grows in cube-face orientation with its crystallographic axes parallel to those of the rock-salt. In general, the silver crystals are twinned repeatedly on all the octahedral faces, and this twinning gives rise to lattice points one-third distance along the cell diagonals of the body-centred reciprocal lattice cell of the silver, thus yielding the so-called 'rational spots' in the diffraction patterns from such silver films. The silver crystals grow in the form of thin lamellae parallel to the {111} planes. This lamellar growth gives rise to spurs from the reciprocal-lattice points, which extend along the cell diagonals normal to the {111} faces. The spurs in turn give rise to the so-called 'irrational spots' in the electron diffraction patterns. The theory has been discussed in detail by von Laue (1948).

An expitaxial deposit will be in a state of strain if the deposited atoms take up positions corresponding to the substrate parameters. Such growths were first observed by Finch and Quarrell (1933, 1934). They noted several examples of 'basal plane pseudomorphism', as they called this phenomenon, and also concluded that this pseudomorphic structure does not persist into and throughout thicker layers, being apparently confined to the first few layers adjoining the substrate. As the film thickness increases, this pseudomorphic strain can be relieved by, *inter alia*, twinning or by rotational slip (Wilman 1950). A well-known example of such twinning is that of silver grown on rock-salt cleavage faces. That this twinning is due to a strain effect is evident for two reasons: (i) the twinning is not found in the surface layers of very thick films (~1000 A.) where the influence of the substrate is lost and Ag grows on Ag without lattice misfit (Kirchner and Cramer 1938); (ii) the twinning disappears only after prolonged heating of the film while in contact with the substrate (Gharpurey 1950), but does so quickly when the detached film is heated and forms a single crystal (Goche and Wilman 1939).

Evans and Wilman (1950) observed a clear example of rotational slip caused by pseudomorphic strain relief in the case of an expitaxial {103} ZnO growth on a ZnS (110) face. The rotational slip occurred on the {110} planes of ZnO which were normal to the substrate surface.

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Recently, Goswami (1950) observed the tadpole-shaped arcing characteristic of rotational slip in some of his electron diffraction patterns and concluded that rotational slip had taken place on {110} planes of Cd in {103} orientation on a (110) face of Cu. Also, Cu_2O in parallel orientation on (110) Cu had slipped rotationally on $(1\bar{1}0)$ planes normal to the substrate surface.

One of us (Gharpurey 1950) obtained an interesting example of rotational slip in the case of Ag deposited on a cleavage face of NaCl at 450° C. The silver was found to be in (110) orientation with $[1\bar{1}0]$ and [001] parallel to the face diagonals of NaCl (001). The lattice misfit along [001] Ag is about 2·5% while that along $[1\bar{1}0]$ of Ag is as high as about 27·5%. The resulting strain gave rise to rotational slip in the Ag crystals on (001) planes normal to the substrate and containing the $[1\bar{1}0]$ rows. The rotations observed were through about 10° and 20°, and the spots due to the rotated crystals were arced, indicating that the (001) lamellae in these rotated crystal fragments had further rotated through small angles, thus relieving the residual strain.

The object of the present work was to study a further example of the stress–structure relationship in expitaxial crystal growth.

§ 2. EXPERIMENTAL

Ag sublimed in vacuo on to a (110) *face of NaCl*

Silver was deposited from a silver filament on to freshly etched (110) and (111) faces of rock-salt kept at 75°–200° C. at a distance of about 8–15 mm. from the filament, the evaporating chamber being evacuated by a rotary pump. The (110) and (111) faces were polished by rubbing along the $[1\bar{1}0]$ direction with successively finer grades of emery paper and finishing with 0000 grade. The faces were etched immediately before use with moist filter paper and then immersed in absolute alcohol. The silver deposits (~100 A. thick) were examined by electron diffraction using a Finch-type camera at 55 kv.

A (110) face of rock-salt consists of alternate $[1\bar{1}0]$ rows of Na and Cl ions. If the silver grew in (110) orientation with [001] silver parallel to $[1\bar{1}0]$ rock-salt and vice versa, the lattice misfit would be small (~2·5%) and the Ag atoms in the junction plane would be in one-to-one correspondence with the ions at the NaCl surface. In spite of this, in all the twenty specimens examined, there was no trace of such an orientation, and the silver always grew in (110) parallel orientation, the lattice misfit being about 27·5%. These results support the view (Drabble 1949) that the epitaxy is such that the nearest possible coordination fit between the AgCl (NaCl type of structure) and Ag structures occurs across the interface. Thus when an Ag atom arrives at the surface, it apparently takes up a position on a $[1\bar{1}0]$ row of NaCl in between two Cl ions (which a Na ion would do if NaCl were continued into space). As more Ag atoms arrive, they pack along this $[1\bar{1}0]$ row of Cl ions and from this a (110) face of Ag develops parallel to the substrate.

Beam along $[1\bar{1}0]$. The diffraction patterns (Figure 1 *) in this azimuth are somewhat similar to those obtained by Cochrane (1936) in the case of Ni electrodeposited on to (110) Cu, and consist of (i) a centred rectangular array $(1 : \sqrt{2})$ of spots with the shorter side of the rectangle parallel to the shadow edge, this being due to the parallel growth of Ag on the (110) face of rock-salt; (ii) two fainter similar patterns rotated each way about the central spot with respect

* For all Figures see Plate at end of issue.

to the above pattern through 70° 34′, and obviously due to twinning on the (111) and (11$\bar{1}$) planes of Ag which are parallel to the beam direction in this azimuth; (iii) lines running through these spots, forming a diamond-shaped network, and due to cross-grating diffractions from (111) and (11$\bar{1}$) twin planes, indicating that the successive twin lamellae are extremely thin and thus virtually act as two-dimensional gratings; and, finally (iv) an elongation of the diffraction spots towards the shadow edge showing that the surface of the Ag crystals is smooth, and an elongation of the twin spots along ⟨112⟩ suggesting development of {112} facets of the twins.

Beam along [001]. The patterns (Figure 2) are similar to those obtained by Cochrane (1936) in the case of Co on (110) Cu. The spot pattern consists of a square network, with one of the diagonals of the square lying parallel to the shadow edge, due to the parallel growth of Ag. Further, receding from the Bragg-reflection position, each spot splits up into four. This indicates, as shown by Cochrane, the development of all the {111} faces, which suggests twinning on all these planes. The greater intensity of the vertical pair of these satellite spots is to be attributed to the greater net surface area of the (111) and (11$\bar{1}$) facets (von Laue 1948).

Arcing of the spots. The diffraction spots were sometimes arced, generally more prominently in the [1$\bar{1}$0] azimuth than in [001]. The arcing was pronounced at lower temperatures and also when the Ag vapour stream was nearly tangential to the surface along [001]. The arcing of the centred rectangular pattern spots ([1$\bar{1}$0] azimuth) is evidently due to the rotation of the Ag crystal lamellae about the [1$\bar{1}$0] axis and thus on (1$\bar{1}$0) planes normal to the substrate surface. The extent of this arcing varied, and in one case (Figures 3 and 4) it was unusually pronounced in the [1$\bar{1}$0] azimuth.

In one of the diffraction photographs with the beam along [1$\bar{1}$0], there was an extra centred rectangular ($1:\sqrt{2}$) network of spots, the unit rectangles being smaller than those due to Ag. Taking $a=4{\cdot}078$ A. for Ag, measurements gave $a=5{\cdot}65$ A. for the unknown substance, which was thus evidently NaCl (5·63) which had sublimed back in parallel orientation on (110) Ag.

Ag sublimed in vacuo on to a (111) *face of NaCl*

The diffraction patterns with the beam along [11$\bar{2}$] of NaCl (for all the four specimens examined) showed (Figure 5) a rectangular ($\sqrt{8}:\sqrt{3}$) network of spots with the longer side parallel to the shadow edge. With the beam along [1$\bar{1}$0] of NaCl, the spot pattern consisted chiefly of two centred rectangular ($1:\sqrt{2}$) patterns with one of the diagonals normal to the shadow edge (Figure 6). Hence the silver had grown in (111) parallel and anti-parallel (i.e. (111)-twin) orientation on rock-salt, i.e. ⟨110⟩Ag‖⟨110⟩NaCl. The parallel growth was always found to be more prominent than the anti-parallel growth. The anti-parallel orientation can be attributed to Ag starting to grow in this orientation at the rock-salt surface, or in parallel orientation and then twinning on the (111) plane parallel to the substrate surface.

There were two fainter centred rectangular ($1:\sqrt{2}$) patterns one of which is due to twinning of 'parallel'-orientated Ag on its (111)-plane, this plane being parallel to the beam in this azimuth. From the three-fold symmetry about the [111] axis, it is clear that the Ag must also have twinned on the (1$\bar{1}$1) and ($\bar{1}$11)

planes. The other rectangular pattern is due to the twinning on the corresponding planes of the Ag crystals in anti-parallel orientation. If all the Ag started to grow in parallel orientation, this twinning on the other octahedral planes of 'anti-parallel' orientated Ag should be absent, as is indicated from the results of deposition of Ag on the cube and (110) faces of rock-salt, where only the initial growths and their twins are found to be present. This suggests that Ag starts growing in both parallel and anti-parallel orientation, there being a greater tendency, however, for parallel growth.

§3. DISCUSSION

Ag was found to grow on suitably heated NaCl (110) and (111) faces in parallel orientation, with twinning on all the {111} faces, in spite of the large lattice difference of about 27·5%. Similarly, in one case NaCl was found to grow in parallel orientation on (110) Ag. As has been mentioned before, silver grown on rock-salt cube faces grows in cube-face parallel orientation with twinning on {111} planes. The twins have their {221} planes parallel to the substrate surface and the ⟨110⟩ rows in these planes parallel to the corresponding ⟨110⟩ rows in the substrate surface. Because of the large lattice differences for parallel growth, Menzer suggested that initially silver grew in {221} orientation, the four equivalent {221} orientations finally becoming parallel as growth proceeded. Carrying this argument further, one would have silver growing with {114} planes parallel to the (110) face of rock-salt and {115} planes parallel to the (111) face. It seems hardly likely that planes with such high indices would develop parallel to the substrate surface; the coordination explanation (Drabble 1949) for parallel growth is more probable.

A new example of rotational slip has been found where silver rotates about a ⟨110⟩ axis. This example coupled with that found previously about a ⟨100⟩ axis (Gharpurey 1950) compares well with that of copper (also face-centred cubic) where Evans and Wilman (1950) found rotational slip taking place about ⟨100⟩, ⟨110⟩, and ⟨111⟩ axes on abrasion, while the translational slip occurs only along $\langle 1\bar{1}0 \rangle$ in a {111} plane.

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Simplified Forms for Free Energy of the Double Layers of Two Plates in a Symmetrical Electrolyte*

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ABSTRACT. Approximate formulae are obtained for the interaction (free) energy of the electric double layers of two parallel plates immersed in an electrolyte of the binary, symmetrical valency type. The three separate simplified expressions which are derived are good approximations at (i) large separations between the plates, (ii) small separations between the plates, and (iii) moderate potentials. The first form is an extension of a result proposed by Verwey and Overbeek in their recent book on the theory of the stability of lyophobic colloids. The third form is a power series in the surface potential, the first term of which is identical with the expression obtained when the linear Debye–Huckel equation in the theory of electrolytes is used. These results are more suitable for numerical computations than the exact formula for the free energy, which is expressed in terms of elliptic integrals.

§1. INTRODUCTION

In their recent book Verwey and Overbeek (1948) consider the interaction of the electric double layers of two parallel plates immersed in a large volume of electrolyte of the binary, symmetrical type. Their formula for the mutual (free) energy is somewhat involved since it entails elliptic integrals, but this is unavoidable if we require the exact expression, which is based on the Poisson–Boltzmann equation. In the present paper, we shall obtain three simpler forms which should be of use in applications to various problems of stability.

We suppose that the two parallel plates, each of unit area, are at separation R and that the edge effects are neglected. Let n be the density of positive (or negative) ions in the bulk of the electrolyte, v the valency of an ion, ϵ the electronic charge, D the dielectric constant of the dispersion medium, T the temperature and $\boldsymbol{k}$ Boltzmann's constant. If ψ is the potential at position x in the double layers, measured in the normal direction from the median plane, then the Poisson–Boltzmann equation reads

$$\frac{d^2\psi}{dx^2} = \frac{8\pi nv\epsilon}{D} \sinh \frac{v\epsilon\psi}{\boldsymbol{k}T}. \qquad \ldots\ldots(1)$$

We shall assume with Verwey and Overbeek that the potential, ψ_0 say, at the surface of each plate ($x = \pm R/2$) is constant, independent of R; ψ_m is the potential at the median plane ($x = 0$). It is convenient to introduce the notation

$$\eta_0 = \epsilon\psi_0/\boldsymbol{k}T, \qquad \eta_m = \epsilon\psi_m/\boldsymbol{k}T, \qquad \ldots\ldots(2a)$$

$$k = \exp(-v\eta_m), \quad \sin\phi_0 = \exp\left\{-\frac{v}{2}(\eta_0 - \eta_m)\right\} = k^{-1/2}\sin\Phi, \qquad \ldots\ldots(2b)$$

$$Z = \sin^2\Phi = \exp(-v\eta_0). \qquad \ldots\ldots(2c)$$

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Then the solution of (1) yields the relation

$$\tfrac{1}{4}\kappa R = k^{1/2}\{K - F(k,\phi_0)\}, \qquad K = F(k,\tfrac{1}{2}\pi), \qquad \ldots\ldots(3)$$

where $\kappa^2 = 8\pi n v^2\epsilon^2/D\boldsymbol{k}T$ is the familiar Debye–Huckel parameter,

$$F(k,\phi_0) = \int_0^{\varphi_0} (1 - k^2\sin^2\phi)^{-1/2}\, d\phi$$

is the elliptic integral of the first kind and K is the corresponding complete integral. The surface charge density σ, which is assumed positive, is given by

$$\sigma = \frac{D}{4\pi}\left(\frac{d\psi}{dx}\right)_{x=R/2} = \frac{\sqrt{2}}{b}(\cosh v\eta_0 - \cosh v\eta_m)^{1/2}, \qquad \ldots\ldots(4)$$

where

$$b = \left(\frac{2\pi}{Dn\boldsymbol{k}T}\right)^{1/2} = \frac{\kappa}{2nv\epsilon}. \qquad \ldots\ldots(4a)$$

Now it is readily shown from the work of Verwey and Overbeek (1948, pp. 78–81) that the free energy associated with the electric double layers of the two plates can be written in the form

$$2F = -4E - 2n\boldsymbol{k}TR(\cosh v\eta_m - 1), \qquad \ldots\ldots(5)$$

where

$$2E = \frac{D}{4\pi}\int_0^{R/2}\left(\frac{d\psi}{dx}\right)^2 dx \qquad \ldots\ldots(6)$$

is the corresponding electrostatic energy of the double layers. A generalized version of (4), applicable to particles of general shape and to electrolytes of any type, will be derived in a following paper. Corkill and Rosenhead (1939) first obtained an expression for E, and if we substitute their result into (4), we obtain precisely the formula for the free energy derived by Verwey and Overbeek, namely

$$2F = -\frac{4n\boldsymbol{k}T}{\kappa}[\tfrac{1}{4}\kappa R(3k^{-1} - 2 - k) + 2(Z + Z^{-1} - k - k^{-1})^{1/2} - 4k^{-1/2}\{E(k,\tfrac{1}{2}\pi) - E(k,\phi_0)\}], \qquad \ldots\ldots(7)$$

where

$$E(k,\phi_0) = \int_0^{\varphi_0}(1 - k^2\sin^2\phi)^{1/2}\, d\phi$$

is the elliptic integral of the second kind. When $R = \infty$, the expression (7) reduces to

$$2F_\infty = -\frac{8n\boldsymbol{k}T}{\kappa}(Z^{1/2} + Z^{-1/2} - 2) = -\frac{32n\boldsymbol{k}T}{\kappa}\sinh^2\frac{v\eta_0}{4}, \qquad \ldots\ldots(8)$$

and we shall denote the change in free energy when the two plates are brought from infinity to position R (under the condition of constant surface potential ψ_0) by

$$V(R) = 2(F - F_\infty). \qquad \ldots\ldots(9)$$

Finally, the derivative of $2F$ with respect to R yields the force equation

$$2\frac{dF}{dR} = -n\boldsymbol{k}T(k + k^{-1} - 2), \qquad \ldots\ldots(10)$$

as shown by Verwey and Overbeek, and originally derived by Langmuir (1938).

§2. INTERACTION ENERGY AT LARGE SEPARATIONS

At large separations $R, \eta_m \simeq 0$ and hence $k \simeq 1, k' \simeq 0$ where k' is the complement of k, given by $k^2 + k'^2 = 1$. This suggests that the expression (7) for the free energy should be expanded in powers of k'. However, this method proves to be laborious and an alternative simpler approach has been adopted. The right-hand side of (3) is expanded in powers of k' and then we are able to invert the resulting series to derive an expansion for k'^2 in terms of $\exp(-\kappa R)$, namely

$$k'^2 = \chi_0 - \tfrac{1}{2}\chi_0^2 + \tfrac{1}{128}(22 - \kappa R - 2\delta)\chi_0^3 + \ldots . \qquad \ldots\ldots(11)$$

where

$$\chi_0 = 16\gamma \exp(-\tfrac{1}{2}\kappa R), \qquad \ldots\ldots(12)$$

$$\gamma = \frac{1 - \sin\Phi}{1 + \sin\Phi} = \tanh\frac{v\eta_0}{4} \qquad \ldots\ldots(13)$$

and

$$\delta = 2\sec^3\Phi \tan\Phi(1 + \sin^2\Phi) = \frac{\cosh v\eta_0/2}{\sinh^2 v\eta_0/2}. \qquad \ldots\ldots(14)$$

The details of the proof of (11) are given in Appendix I. A simple interpretation can be given to the first term in the series (11) for k'^2, i.e. to the approximation $k'^2 = \chi_0$: at very large R, $\eta_m \simeq 0$ and k'^2 can be written as

$$k'^2 = 1 - \exp(-2v\eta_m) \simeq 2v\eta_m.$$

Thus (11) becomes

$$v\eta_m = ve\psi_m/\boldsymbol{k}T \simeq 8\gamma \exp(-\tfrac{1}{2}\kappa R) \qquad \ldots\ldots(11\,a)$$

very nearly. This is precisely the form assumed by Verwey and Overbeek (1948, equation (33), p. 70), who showed that (11 *a*) implies that the electrical potential at the median plane is obtained by superposing the separate potentials of the two double layers.

The right-hand member of the force equation (10) is now expanded in powers of k'; then integrating with respect to R, we derive

$$2F = 2F_\infty - \tfrac{1}{4}n\boldsymbol{k}T \int_\infty^R (k'^4 + k'^6 + \tfrac{15}{16}k'^8 + \ldots)\,dR. \qquad \ldots\ldots(15)$$

Substituting (11) into the integrand on the right of (15), the first three terms in the series obtained for $2F$ read

$$2F = 2F_\infty + V_2(R) + \ldots . \qquad \ldots\ldots(16)$$

where we introduce the notation

$$V_1(R) = \frac{n\boldsymbol{k}T}{4\kappa}\chi_0^2, \qquad \ldots\ldots(17\,a)$$

$$V_2(R) = V_1(R)\{1 + \mathscr{C}(v\eta_0, \kappa R)\}, \qquad \ldots\ldots(17\,b)$$

$$\mathscr{C}(v\eta_0, \kappa R) = -\tfrac{1}{256}\chi_0^2(2\kappa R - 3 + 4\delta) = \mathscr{C}, \text{ say.} \qquad \ldots\ldots(18)$$

$2F_\infty$ is given by (8) and γ and δ are defined by (13) and (14) respectively. Verwey and Overbeek obtained the approximation $V_1(R)$ for the change in free energy $V(R)$ (defined by (9)), by using the physical argument that the potentials for the double layers of two single plates can be added linearly at the median plane, if the separation R is large.

Although in deriving (15) we have assumed the surface potential ψ_0 to be constant, independent of R, our formula for $2F$ can still be used in the more general case where ψ_0 varies with R. For we can treat ψ_0 as a parameter and express the free energy $2F$ and the surface charge density σ as functions of ψ_0

and R. Thus, the expansion of the right-hand side of (4) in powers of k' and the subsequent substitution of (11) yields

$$\sigma = \frac{4\pi v\epsilon}{\kappa} \sinh \frac{v\eta_0}{2} \left[1 - \frac{1}{32 \sinh^2 \frac{1}{2} v\eta_0} \left(k'^4 + k'^6 + \tfrac{15}{16} k'^8 + \frac{1}{64 \sinh^2 \frac{1}{2} v\eta_0} k'^8 + \ldots \right) \right]$$

$$= \frac{4\pi v\epsilon}{\kappa} \sinh \frac{v\eta_0}{2} \left[1 - \frac{\chi_0^2}{32 \sinh^2 \frac{1}{2} v\eta_0} \left\{ 1 + \tfrac{1}{64} \chi_0^2 \left(2 - \kappa R - 2\delta + \frac{1}{\sinh^2 \frac{1}{2} v\eta_0} \right) + \ldots \right\} \right]. \quad \ldots\ldots(19)$$

Now Casimir (1948) has shown that the form (7) for the free energy can be expressed as

$$2F = -2 \int_0^{\psi_0} \sigma' \, d\psi' = -2 \frac{kT}{\epsilon} \int_0^{\eta_0} \sigma' \, d\eta', \quad \ldots\ldots(20)$$

where ψ' is the surface potential which is imagined to vary from 0 to its actual value ψ_0 and $\eta' = \epsilon\psi'/kT$. To obtain the form of σ' (which is a function of η') in the integrand of (20), we need only replace η_0 by η' in (19). However, it follows from the considerations of Derjaguin (1940), Verwey and Overbeek (1948) and one of the present authors (Levine 1946, 1948, 1950 a, b) that when ψ_0 varies with R, we should work with the so-called 'electrical' part of the free energy associated with the double layers, namely

$$2F^* = 2 \int_0^{\sigma} \psi' \, d\sigma' = 2\psi_0\sigma + 2F. \quad \ldots\ldots(21)$$

The expression for $2F^*$ as a function of ψ_0 and R is immediately derived from (16) and (19). The method of obtaining the variation of ψ_0 with R is explained in the earlier papers by Levine referred to above. Briefly, the condition that the total free energy ('electrical' energy, 'chemical' energy and 'configurational' energy associated with the adsorbed layers of ions on the plates) of our system of two plates in an electrolyte is a minimum yields a relation between ψ_0 and R. In a later publication, we shall make use of the formulae obtained in this paper to determine the latter relation for particular mechanisms of adsorption of ions on the plates.

Now Verwey and Overbeek (1948, p. 95) remark that it is "impossible" to integrate the general expression for the force between the particles with respect to the distance and "hence there is no advantage in using this force equation to evaluate the repulsive potential for a system of two plane double layers, on the basis of the complete differential equation" (1). However, the preceding method does carry through the integration of the force equation (10) at large separations. In principle, it is quite possible to determine the higher terms in the expansion (16), but this is found to be very laborious, and work is now in progress on a possibly simpler approach which entirely avoids the use of elliptic integrals. The region of convergence of (16) will not be investigated in the present paper.

We shall restrict the numerical calculations of our free-energy expression (16) to the case where ψ_0 is constant, independent of R. The severest test of the approximations (17 *a*) and (17 *b*) for $V(R)$ is, of course, at contact of the plates. Now when $R=0$, $F=0$ since the surface charge density vanishes under the condition of constant surface potential ψ_0, and it follows from (9) that the exact value of $V(0)$ is $-2F_\infty$. We therefore derive from (8) and (17 *a*) that the ratio

$$V_1(0)/V(0) = 2 \operatorname{sech}^2 v\eta_0/4$$

which is plotted as a function of $v\eta_0$ in Figure 1. We also show the corresponding plot of $V_2(0)/V(0)$. It is seen that the second approximation $V_2(0)$ is worse than the first in the vicinity of $v\eta_0 = 4$.

At sufficiently large separations $V_2(R) < V_1(R)$ and since we can assume that the difference $|V_2(R) - V(R)|$ is much less than $|V_1(R) - V(R)|$, it follows that $V(R) < V_1(R)$. This is consistent with the curves for $V(R)$ and $V_1(R)$ as functions of R, which were calculated by Verwey and Overbeek (1948, Figure 17, p. 85). Now $V_1(0) = V(0)$ at $v\eta_0 \simeq 3{\cdot}53$; for smaller $v\eta_0$, $V_1(0) > V(0)$ and for larger $v\eta_0$, $V_1(0) < V(0)$. It follows that the curves for $V(R)$ and $V_1(R)$ must cross each other when $v\eta_0 \geqslant 3{\cdot}53$.

Verwey and Overbeek have suggested that the first term $V_1(R)$ is a satisfactory approximation when $\kappa R > 2$. In Figure 2, we show the variation of the 'correction' term $\mathscr{C} = \mathscr{C}(v\eta_0, \kappa R)$ with $v\eta_0$ at $\kappa R = \frac{1}{2}$, 1 and 2. We observe that when $\kappa R = 2$, $\mathscr{C}$ is at most 0·17 (approximately). At $\kappa R = 1$, $\mathscr{C} \simeq -0{\cdot}37\,(=e^{-1})$ when $\eta_0 = 0$ and $\mathscr{C} \to 0{\cdot}37$ as $\eta_0 \to \infty$. When $\kappa R = \frac{1}{2}$, then $\mathscr{C} \simeq -0{\cdot}61\,(=e^{-1/2})$ at $\eta_0 = 0$ and $\mathscr{C} \to 1{\cdot}21 (2e^{-1/2})$ as $\eta_0 \to \infty$.

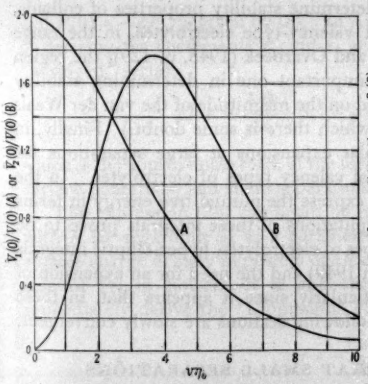

Figure 1. Ratios $V_1(0)/V(0)$ (curve A) and $V_2(0)/V(0)$ (curve B) as functions of $v\eta_0$.

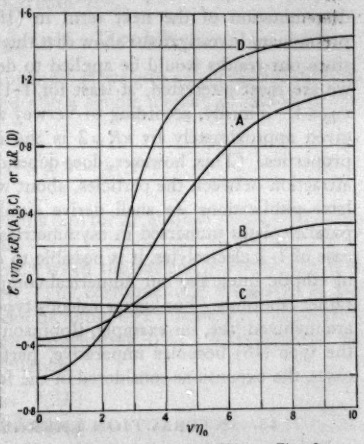

Figure 2. Correction term $\mathscr{C}(v\eta_0, \kappa R)$ as function of $v\eta_0$. A: $\mathscr{C}(v\eta_0, \frac{1}{2})$; B: $\mathscr{C}(v\eta_0, 1)$; C: $\mathscr{C}(v\eta_0, 2)$; D: values of κR at which $\mathscr{C}(v\eta_0, \kappa R) = 0$.

To illustrate further the behaviour of $V_1(R)$ and $V_2(R)$, we have computed in Table 1 the values of $V_1(R)/V(0) = 2\,\mathrm{sech}^2(v\eta_0/4)\exp(-\kappa R)$ and of

$$V_2(R)/V(0) = \{V_1(R)/V(0)\}(1 + \mathscr{C})$$

at $\kappa R = \frac{1}{2}$, 1, 2 and $v\eta_0 = 2$, 4, 6 and 8. These are compared with the values of $V(R)/V(0)$ as determined (by interpolation) from Verwey and Overbeek (1948, Table XI, p. 82) shown as $[V(R)/V(0)]_{V,O}$. (The third figure in these interpolated quantities can only be estimated.) We see that the second approximation is more accurate than the first at $\kappa R = 2$ and at $\kappa R = 1$ if $v\eta_0 \leqslant 4$. However, the opposite is the case at $\kappa R = 1$, $v\eta_0 = 6$ and 8 and at $\kappa R = \frac{1}{2}$, $v\eta_0 = 4$ and 6. The

reason for this behaviour can be traced to the fact that the curves for $V_1(R)$ and $V(R)$ cross each other. For example, when $v\eta_0=6$, the crossing-point is close to $\kappa R=1$.

Table 1. First and Second Approximations at Large Separations

	$V_1(R)/V(0)$			$V_2(R)/V(0)$			$[V(R)/V(0)]_{V,0}$		
$v\eta_0$ \ κR	$\frac{1}{2}$	1	2	$\frac{1}{2}$	1	2	$\frac{1}{2}$	1	2
2	0·955	0·579	0·213	0·649	0·421	0·179	$0{\cdot}70_0$	$0{\cdot}45_7$	$0{\cdot}18_6$
4	0·510	0·309	0·114	0·664	0·300	0·0945	$0{\cdot}51_8$	0·28	0·098
6	0·219	0·133	0·0489	0·384	0·157	0·0413	$0{\cdot}28_8$	$0{\cdot}13_3$	0·042
8	0·0857	0·0520	0·0191	0·176	0·0672	0·0164	$0{\cdot}13_0$	$0{\cdot}054_3$	0·017

From the preceding considerations it might appear that the series expansion (16) is of rather doubtful value. However, in the opinion of the authors this is not the case for the following reasons. Firstly, the forms of the terms evaluated above in (16) are quite simple and amenable to numerical computations. The determination of the next term in (16) would increase the usefulness, and preliminary investigations show that this term is not too complicated. Secondly, since our results would be applied to determine stability properties of colloids, we are most interested, at least for 1–1 valency-type electrolytes, in the range $v\eta_0\leqslant 4$. Thirdly, according to Verwey and Overbeek (1948, p. 129), the region given approximately by $\kappa R\geqslant 2$ is the important one in determining stability properties. (This, however, does depend on the magnitude of the van der Waals attraction between the particles, about which there is some doubt.) Finally, in later publications we shall derive similar expansions at large separations for parallel plates immersed in asymmetrical valency types of electrolytes. In the case of 1–2 electrolytes, it is possible to express the mutual free energy in terms of elliptic integrals, but numerical computations of these integrals prove to be rather laborious. For higher valency types of electrolytes, hyper-elliptic integrals are involved (see, for example, Robinson 1949) and the need for an expansion of the type (16) becomes imperative, particularly since it appears that, in these cases, the expansions considered in the following sections are slowly convergent.

§ 3. INTERACTION ENERGY AT SMALL SEPARATIONS

When $R\to 0$, $\psi_m\to\psi_0$ and hence $k\to Z$. This suggests that we work in terms of $w^2=k/Z-1$, noting that $k>Z$. It is possible to expand the free-energy expression (7) in powers of w, but, as in the previous section, a simpler approach is to integrate the force equation (10). To carry this out, we first express the right-hand member of (3) in powers of w and then revert the series to obtain

$$w=(1-Z^2)^{1/2}S[1-\tfrac{1}{6}(1+4Z^2)S^2+\tfrac{1}{5}(\tfrac{7}{8}+\tfrac{1}{6}Z^2+4Z^4)S^4+\ldots.], \quad \ldots\ldots(22)$$

where

$$S=\frac{\kappa R}{4Z^{1/2}}=\tfrac{1}{4}\kappa R\exp(v\eta_0/2). \quad \ldots\ldots(23)$$

The derivation of (22) is given in Appendix II. Noting that $k=(1+w^2)Z$, the equation (10) can be written as

$$2\frac{dF}{dR}=-\frac{nkT}{Z}[(1-Z)^2-(1-Z^2)w^2+w^4-w^6+\ldots.]. \quad \ldots\ldots(10\,a)$$

Making use of (22), the relation (10 *a*) becomes

$$2\frac{dF}{dS} = -\frac{4nkT}{\kappa Z^{1/2}}(1-Z)^2[1-(1+Z)^2S^2+\tfrac{4}{3}(1+Z)^2(1+Z^2)S^4 - \tfrac{92}{45}(1+Z)^2(1+\tfrac{22}{23}Z^2+Z^4)S^6+\ldots.]. \qquad \ldots\ldots(24)$$

The series expansion for F in powers of S or κR is immediately derived from

$$2F = 2\int_0^R \frac{dF}{dR}\,dR = 2\int_0^S \frac{dF}{dS}\,dS, \qquad \ldots\ldots(25)$$

noting that $F=0$ when $R=0$. We now substitute (24) into (25) and make use of (2 *c*) and (23), so that F is expressed in terms of η_0 rather than Z. Integration of (25) yields

$$\begin{aligned} 2F &= V(R)-V(0) \\ &= V(0)[-\alpha_1\kappa R+\alpha_3(\kappa R)^3-\alpha_5(\kappa R)^5+\alpha_7(\kappa R)^7+\ldots.], \qquad \ldots\ldots(26) \end{aligned}$$

where $\alpha_1 = \frac{1}{2}\cosh^2\frac{1}{4}v\eta_0$, $\quad \alpha_3 = \frac{1}{12}\alpha_1\cosh^2\frac{1}{2}v\eta_0$,

$$\alpha_5 = \tfrac{1}{10}\alpha_3\cosh v\eta_0, \quad \alpha_7 = \tfrac{1}{3360}\alpha_3(11+23\cosh 2v\eta_0), \qquad \ldots\ldots(27)$$

and $V(0) = -2F_\infty$ is given by (8). In Appendix II we give an alternative method of deriving the coefficients α_1 and α_3 and also a simple method of obtaining the 'abridged' series

$$2F = -\frac{4nkT}{\kappa Z^{1/2}}S(1-\tfrac{1}{3}S^2+\tfrac{4}{15}S^4-\tfrac{92}{315}S^6+\ldots.), \qquad \ldots\ldots(28)$$

which is the approximate form of the formula (26) for $2F$ at small values of Z (large surface potentials) and small separations.

The expression (26) can again be used when the surface potential ψ_0 varies with R by regarding ψ_0 as a parameter. The corresponding expansion of the surface charge density in powers of κR can be found by expressing the right-hand side of (4) in powers of w and then substituting (22). Alternatively, we immediately derive the 'Lippmann' equation

$$\sigma = -\frac{v\epsilon}{2kT}\frac{\partial(2F)}{\partial(v\eta_0)} \qquad \ldots\ldots(20\,a)$$

from (20). On substituting (26) for $2F$, the required series for σ is

$$\begin{aligned} \sigma = \frac{nv\epsilon}{\kappa}\kappa R\sinh v\eta_0\Big[&1-\tfrac{1}{12}\cosh v\eta_0(\kappa R)^2 \\ &+\tfrac{1}{480}(3\cosh 2v\eta_0+1)(\kappa R)^4 \\ &-\frac{1}{64\times 315}\cosh v\eta_0(23\cosh 2v\eta_0-6)(\kappa R)^6+\ldots.\Big]. \qquad \ldots\ldots(29) \end{aligned}$$

A detailed study of the radius of convergence, $(\kappa R)_0$ say, of the expansion (26) will be deferred to a later paper. However, an examination of the terms in (26) suggests the following behaviour. As $\eta_0\to 0$, $(\kappa R)_0\to\pi$; when $v\eta_0>1$ approximately, a lower bound for $(\kappa R)_0$ seems to be $(\kappa R)_l = \pi/\cosh^{1/2}v\eta_0$; an upper bound is probably $(\kappa R)_u = \pi/\cosh\frac{1}{2}v\eta_0$. In Table 2 we have calculated $(\kappa R)_l$ and $(\kappa R)_u$ for various $v\eta_0$. The range of κR in which the series (27) is useful is,

however, smaller than that defined by the lower bound. In Table 3 we compute the terms in the square brackets in (26) for the conveniently chosen value $\kappa R \simeq \frac{2}{3}(\kappa R)_l$, which is an estimate of the range of application of (26). Comparison with the exact value of $V(R)/V(0)$, as estimated (by interpolation) from Verwey and Overbeek's Table XI, shows that the first five terms in (26) yield fairly accurate results, the error being 1 or 2%. For large $v\eta_0 (>8)$, $(\kappa R)_l$ is so small that the expansion (26) is of limited use.

Table 2. Region of Convergence of Expansion at Small Separations

$v\eta_0$	1	2	3	4	5	6	8	10
Lower bound $(\kappa R)_l$	2·53	1·63	0·99	0·60	0·36	0·22	0·081	0·0095
Upper bound $(\kappa R)_u$	2·79	2·03	1·33	0·83	0·51	0·31	0·11	0·042

Table 3. Values of Terms in Expansion at Small Separations

$v\eta_0$	$\kappa R \simeq \frac{2}{3}(\kappa R)_l$	$\alpha_1 \kappa R$	$\alpha_3(\kappa R)^3$	$\alpha_5(\kappa R)^5$	$\alpha_7(\kappa R)^7$	$V(R)/V(0)$ Eqn. (27)	$[V(R)/V(0)]_{V,0}$
2	1·0	0·6360	0·1262	0·0475	0·0240	0·467	$0·45_7$
4	0·4	0·4762	0·0899	0·0393	0·0235	0·598	$0·58_9$
6	0·15	0·4150	0·0789	0·0358	0·0223	0·650	$0·64_3$

§4. INTERACTION ENERGY AT MODERATE POTENTIALS

Gronwall, La Mer and Sandved (1929) originally solved the Poisson–Boltzmann equation in the case of a spherical particle (or rather ion) by the method of Green's function and obtained a solution for the potential in the form of a power series in the surface charge. Recently Booth (1950) applied this method to two parallel plates. However, it is possible to develop a series expansion for the potential ψ_0 by starting with the solution (3). The latter is written as

$$\exp\left\{-\frac{v}{2}(\eta_0-\eta_m)\right\} = \sin\phi_0 = \mathrm{sn}\,(K-u,k)$$

$$= \frac{\mathrm{cn}\,(u,k)}{\mathrm{dn}\,(u,k)} = \frac{1}{\mathrm{dn}\,(iu,k')}, \qquad \ldots\ldots(30)$$

where

$$u = \tfrac{1}{4}\kappa R k^{-1/2}, \qquad \ldots\ldots(31)$$

and we have introduced the usual notation for the Jacobian elliptic functions. The second, third and fourth relations in (30) are well-known properties of these functions. It follows that

$$v\eta_0 = v\eta_m + 2\ln \mathrm{dn}\,(iu,k'). \qquad \ldots\ldots(30\,a)$$

To obtain an expansion of η_m in powers of η_0, we make use of the infinite product formula for the Jacobian elliptic function $\mathrm{dn}\,(iu,k')$, and it is shown in Appendix III that we can derive the series

$$v\eta_m = v\eta_0 \,\mathrm{sech}\,\tfrac{1}{2}\kappa R - (v\eta_0)^3 g(\tfrac{1}{2}\kappa R) + (v\eta_0)^5 h(\tfrac{1}{2}\kappa R) + \ldots. \qquad \ldots\ldots(32)$$

from (30 *a*), where the functions g and h are given by

$$\left.\begin{aligned} g(x) &= \tfrac{1}{16}\tanh x \,\mathrm{sech}\, x(x\,\mathrm{sech}^2 x + \tfrac{1}{3}\tanh x),\\ h(x) &= \frac{1}{2(16)^2}\,\mathrm{sech}\, x[x^2\,\mathrm{sech}^4 x(5-6\,\mathrm{sech}^2 x)\\ &\quad + \tfrac{1}{2}x\tanh x\,\mathrm{sech}^2 x(4-7\,\mathrm{sech}^2 x) + \tfrac{1}{30}\tanh^2 x(8+3\,\mathrm{sech}^2 x)]. \end{aligned}\right\} \qquad \ldots\ldots(33)$$

The expansion of (4) in powers of η_0 and η_m leads to

$$b^2\sigma^2 = v^2(\eta_0^2 - \eta_m^2) + \tfrac{1}{12}v^4(\eta_0^4 - \eta_m^4) + \tfrac{1}{360}v^6(\eta_0^6 - \eta_m^6) + \dots ,$$

and on substitution of (30 *a*), we derive

$$b\sigma = v\eta_0 \tanh \tfrac{1}{2}\kappa R + (v\eta_0)^3 G(\tfrac{1}{2}\kappa R) + (v\eta_0)^5 H(\tfrac{1}{2}\kappa R) + \dots , \quad \dots\dots(34)$$

where

$$\left.\begin{aligned} G(x) &= \tfrac{1}{48}[3x \operatorname{sech}^4 x + \tanh x(2 + 3\operatorname{sech}^2 x)], \\ H(x) &= \frac{1}{(32)^2}[-12x^2 \tanh x \operatorname{sech}^6 x - x \operatorname{sech}^4 x(8 - 15\operatorname{sech}^2 x) \\ &\quad + \tanh x(\tfrac{8}{15} - 2\operatorname{sech}^2 x + 3\operatorname{sech}^4 x)]. \end{aligned}\right\} \quad \dots\dots(35)$$

To determine the free energy, we make use of (20), replacing η_0 by η' in (34) to obtain σ'. Substituting (4 *a*) for *b*, we derive

$$\left.\begin{aligned} 2F = -\frac{2nkT}{\kappa}(v\eta_0)^2[\tanh \tfrac{1}{2}\kappa R + \tfrac{1}{2}(v\eta_0)^2 G(\tfrac{1}{2}\kappa R) \\ + \tfrac{1}{3}(v\eta_0)^4 H(\tfrac{1}{2}\kappa R) + \dots .]. \end{aligned}\right\} \quad \dots\dots(36)$$

The corresponding expression for $2F_\infty$ is obtained from (8) and reads

$$2F_\infty = -\frac{2nkT}{\kappa}(v\eta_0)^2[1 + \tfrac{1}{48}(v\eta_0)^2 + \tfrac{1}{5760}(v\eta_0)^4 + \dots .]. \quad \dots\dots(8\,a)$$

If we retain the first term only on the right of (36) and (8 *a*), a first approximation to the interaction energy (9) is obtained, namely

$$V_I(R) = \frac{2nkT}{\kappa}(v\eta_0)^2(1 - \tanh \tfrac{1}{2}\kappa R), \quad \dots\dots(37\,a)$$

which follows when the linear Debye–Huckel equation replaces the Poisson–Boltzmann equation (1). Second and third approximations to $V(R)$ are written as

$$\left.\begin{aligned} V_{II}(R) &= V_I(R)[1 + (v\eta_0)^2 G^*(\tfrac{1}{2}\kappa R)], \\ V_{III}(R) &= V_{II}(R) + V_I(R)(v\eta_0)^4 H^*(\tfrac{1}{2}\kappa R), \end{aligned}\right\} \quad \dots\dots(37\,b)$$

where $$G^*(x) = \frac{1}{48}\frac{1 - 24G(x)}{1 - \tanh x}, \quad H^*(x) = \frac{1}{5760}\frac{1 - 1920H(x)}{1 - \tanh x}. \quad \dots\dots(38)$$

We can also write (36) as

$$2F = -V_I(R)[1 + \tfrac{1}{2}(v\eta_0)^2 \coth \tfrac{1}{2}\kappa R \,.\, G(\tfrac{1}{2}\kappa R) + \tfrac{1}{3}(v\eta_0)^4 \coth \tfrac{1}{2}\kappa R \,.\, H(\tfrac{1}{2}\kappa R) + \dots]. \quad \dots\dots(36\,a)$$

If we expand (16) and (36) in powers of η_0^2 and $\exp(-\frac{1}{2}\kappa R)$ respectively, then both formulae lead to the same double series in η_0^2 and $\exp(-\frac{1}{2}\kappa R)$. In a similar fashion, expansion of (26) and (36) in powers of η_0^2 and κR respectively leads to the same double series in η_0^2 and κR. Thus in each case, we arrive at the same result by two entirely different approaches, which is a confirmation of the validity of the expansions developed in this paper. We have also verified the series (37) by the method of Green's function referred to above.

The formulae (37) for the free energy apply when ψ_0 is independent of R. However, we can also use these results in the general case when ψ_0 varies with R, just as in the preceding sections. We need only work with (34) and (36) simultaneously, regarding σ and $2F$ as functions of ψ_0 and κR. If the surface potential ψ_0 is not too large, we can invert the series (34) for σ and then express $2F$

in powers of σ. (This, indeed, is the form of the solution of the Poisson–Boltzmann equation by the method of Green's function.) However, it seems that the expansion of $2F$ in powers of σ has a smaller radius of convergence than the corresponding expansion in powers of ψ_0. To illustrate this behaviour, we consider the case of infinite separation of the plates, when the relation (4) becomes

$$b\sigma = 2\sinh\tfrac{1}{2}v\eta_0 \qquad \text{or} \qquad v\eta_0 = 2\sinh^{-1}\tfrac{1}{2}b\sigma. \qquad \ldots\ldots(39)$$

Making use of (20) and (39), we find that the series (8 *a*) for $2F_\infty$ converges for all values of ψ_0, whereas the series for $2F_\infty$ in powers of σ has a radius of convergence $|b\sigma/2| = 1$ or $|v\eta_0| = 1{\cdot}763$.

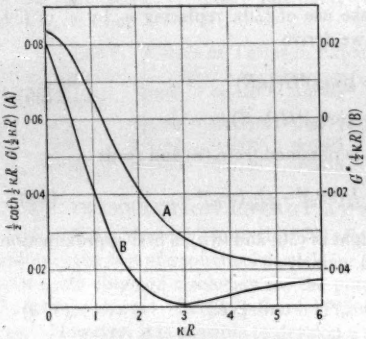

Figure 3. Plots of $\frac{1}{2}\coth\frac{1}{2}\kappa R\,.\,G(\frac{1}{2}\kappa R)$ (curve A) and of $G^*(\frac{1}{2}\kappa R)$ (curve B) as functions of κR.

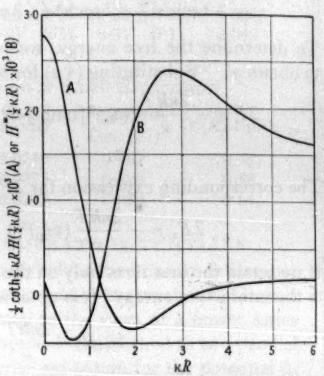

Figure 4. Plots of $\frac{1}{2}\coth\frac{1}{2}\kappa R\,.\,H(\frac{1}{2}\kappa R)$ (curve A) and of $H^*(\frac{1}{2}\kappa R)$ (curve B) as functions of κR.

Table 4. Values of Functions $G(\frac{1}{2}\kappa R)$ and $H(\frac{1}{2}\kappa R)$

κR	$G(\frac{1}{2}\kappa R)\times10^2$	$H(\frac{1}{2}\kappa R)\times10^3$	κR	$G(\frac{1}{2}\kappa R)\times10^3$	$H(\frac{1}{2}\kappa R)\times10^3$	κR	$G(\frac{1}{2}\kappa R)\times10^2$	$H(\frac{1}{2}\kappa R)\times10^3$
0	0	0	1·4	6·678	−0·1897	3·6	4·678	0·1699
0·1	0·8306	0·4112	1·5	6·683	−0·3887	3·8	4·583	0·2420
0·2	1·645	0·7896	1·6	6·650	−0·5472	4·0	4·505	0·2996
0·3	2·427	1·107	1·7	6·586	−0·6640	4·2	4·441	0·3453
0·4	3·163	1·342	1·8	6·498	−0·7406	4·4	4·389	0·3814
0·5	3·840	1·479	1·9	6·393	−0·7805	4·6	4·348	0·4099
0·6	4·450	1·515	2·0	6·275	−0·7885	4·8	4·314	0·4324
0·7	4·987	1·447	2·2	6·228	−0·7302	5·0	4·286	0·4502
0·8	5·445	1·314	2·4	5·761	−0·6078	5·2	4·264	0·4643
0·9	5·826	1·107	2·6	5·515	−0·4599	5·4	4·246	0·4754
1·0	6·130	0·8563	2·8	5·294	−0·3007	5·6	4·231	0·4843
1·1	6·361	0·5829	3·0	5·100	−0·1553	5·8	4·219	0·4914
1·2	6·525	0·3069	3·2	4·934	−0·02915	6·0	4·209	0·4970
1·3	6·628	0·04510	3·4	4·794	0·08084	∞	4·167	0·5208

Table 4 gives the values of the functions $G(\frac{1}{2}\kappa R)$ and $H(\frac{1}{2}\kappa R)$ for various κR. In Figure 3, we have plotted $\frac{1}{2}\coth\frac{1}{2}\kappa R\,.\,G(\frac{1}{2}\kappa R)$ and $G^*(\frac{1}{2}\kappa R)$ as functions of κR, and in Figure 4, $\frac{1}{2}\coth\frac{1}{2}\kappa R\,.\,H(\frac{1}{2}\kappa R)$ and $H^*(\frac{1}{2}\kappa R)$. It is seen that the maximum values of the magnitude of $G^*(\frac{1}{2}\kappa R)$ and $H^*(\frac{1}{2}\kappa R)$ are approximately 0·049 and 0·0024 respectively. Now the usual comment is that $V_I(R)$ is a good approximation if $v\eta_0 \ll 1$. However, when $v\eta_0 = 1$ ($\psi_0 = 25$ millivolts for a uni-univalent electrolyte at room temperature) the correction factor $(v\eta_0)^2 G^*(\frac{1}{2}\kappa R)$ is less than about 2% in the range $0 < \kappa R < 1$ and is never greater than 5% for larger

κR; the next term $(v\eta_0)^4 H^*(\frac{1}{2}\kappa R)$ is less than 0·25%. It is true, however, that these corrections increase rapidly with surface potential, being proportional to ψ_0^2 and ψ_0^4 respectively. In Table 5, we have computed the ratios $V_I(R)/V(0)$, $V_{II}(R)/V(0)$ and $V_{III}(R)/V(0)$ for various $v\eta_0$ and κR. These are to be compared with the values of $V(R)/V(0)$ which are derived from Verwey and Overbeek's Table XI, or from the series (26) when κR is small.

Table 5. First, Second and Third Approximations at Moderate Potentials

	$V_I(R)/V(0)$				$V_{II}(R)/V(0)$			
$v\eta_0$ \ κR	0	$\frac{1}{2}$	1	2	0	$\frac{1}{2}$	1	2
1	0·9794	0·7395	0·5268	0·2335	0·9998	0·7411	0·5172	0·2232
2	0·9207	0·6952	0·4952	0·2195	0·9974	0·7012	0·4591	0·1807
3	0·8318	0·6281	0·4474	0·1983	0·9878	0·6403	0·3740	0·1194
4	0·7241	0·5467	0·3895	0·1726	0·9654	0·5656	0·2758	0·0505

	$V_{III}(R)/V(0)$				$[V(R)/V(0)]_{V,O}$			$V(R)/V(0)$ Eqn. (26)	
$v\eta_0$ \ κR	0	$\frac{1}{2}$	1	2	$\frac{1}{2}$	1	2	$\frac{1}{2}$	1
1	1·0000	0·7408	0·5171	0·2236	$0·77_6$*	$0·55_3$*	$0·22_4$	0·741	0·517
2	1·0000	0·6965	0·4574	0·1871	$0·70_0$	$0·45_7$	$0·18_6$	0·697	0·467
3	0·9995	0·6188	0·3665	0·1488	$0·62_1$	$0·37_2$	$0·13_0$	0·621	—
4	0·9976	0·5064	0·2550	0·1314	$0·51_6$	0·28	0·098	—	—

* These values must be incorrect. We find that a number of the values of $V(R)$ at $v\eta_0=1$, in Verwey and Overbeek's Table XI, are in error.

When $v\eta_0=1$ and 2, the second approximation $V_{II}(R)$ is better than the first $V_I(R)$. We observe, however, that for $v\eta_0=3$ and 4 and $\kappa R=\frac{1}{2}$, $V_I(R)$ is closer to $V(R)$ than $V_{II}(R)$. To explain this behaviour of $V_I(R)$, we compare $V(R)$ with $V_I(R)$ when $\kappa R=0$ and $\kappa R \gg 1$. Since $V(0)=-2F_\infty$, which is given by (8), we readily verify that $V(0)>V_I(0)$ for all $\eta_0>0$. If we put $2\exp(-\kappa R)$ for $1-\tanh\frac{1}{2}\kappa R$ in the expression for $V_I(R)$ and assume that $V(R)$ can be replaced by $V_I(R)$, (defined by (17*a*)), then it follows that for large κR, $V(R)<V_I(R)$. This means that for any given η_0, the curves for $V(R)$ and $V_I(R)$, plotted as functions of κR, must cross at some κR. The form of the function $H^*(\frac{1}{2}\kappa R)$, which is zero in the vicinity of $\kappa R=0·55$, suggests that this intersection point is close to $\kappa R=0·55$. Thus we can readily understand why $V_I(R)$ is a better approximation than $V_{II}(R)$ at $\kappa R=\frac{1}{2}$. The general conclusions of the results shown in Figures 3 and 4 and in Table 5 are as follows. For $v\eta_0 \leqslant 2$, $V_{II}(R)$ differs from $V(R)$ by 2 or 3% at the most; this difference is particularly small if $\kappa R \ll 1$. The accuracy of $V_{III}(R)$ cannot be checked with any reliability, since the values of $V(R)$ interpolated from Verwey and Overbeek's Table XI are not sufficiently exact; $V_{III}(R)$ differs from $V(R)$ perhaps in the fourth figure. For $v\eta_0=3$, the error in $V_{II}(R)$ is less than about 10%; $V_{III}(R)$ is more accurate than $V_{II}(R)$ for $\kappa R \leqslant \frac{1}{2}$, but this is no longer true for $\kappa R \geqslant 1$. In the latter range of κR, the series (37) seems to be converging slowly and the use of our expansion (16) in §2 should be more useful, particularly when the next term in (16) has been determined. For higher potentials the latter behaviour of (37) is even more accentuated and the evaluation of the higher terms would be desirable; this is quite straightforward but will not be given here.

APPENDIX I

To derive the series (11) for k'^2, we proceed as follows. If $k' \tan\phi_0 < 1$, then

$$F(k,\phi_0) = \int_0^{\phi_0} \frac{d\phi}{\cos\phi(1+k'^2\tan^2\phi)^{1/2}} \qquad \ldots\ldots(A\,1)$$

$$= -\tfrac{1}{2}\ln\gamma - \tfrac{1}{8}\ln\gamma\,.k'^2 + \tfrac{1}{128}(\delta - 9\ln\gamma)k'^4 + \ldots\,, \qquad \ldots\ldots(A\,1\,a)$$

where γ and δ are defined in (13) and (14) respectively.

In outlining the proof of this result, we shall simplify the notation by omitting the subscript zero on ϕ_0. We put $t = k'^2$ and regard $F(k,\phi)$ as a function of t and ϕ, say $F(k,\phi) = L(t,\phi)$. Further, ϕ is a function of t, which is obtained from $(2\,b)$, namely

$$\phi = \sin^{-1}\{(1-t)^{-1/4}\sin\Phi\}. \qquad \ldots\ldots(2\,d)$$

We now expand $L = L(t,\phi)$ in a Taylor series about $t = 0$,

$$L(t,\phi) = L(0,\Phi) + t(L_t + \phi' L_\varphi)_{t=0} + \tfrac{1}{2}t^2(L_{tt} + 2\phi' L_{t\varphi} + \phi'^2 L_{\varphi\varphi} + \phi'' L_\varphi)_{t=0} + \ldots\,, \qquad \ldots\ldots(A\,1\,b)$$

noting that $\phi = \Phi$ at $t = 0$. Here the subscripts t and ϕ denote partial derivatives, and ϕ' and ϕ'' are the first and second derivatives of ϕ with respect to t. The various derivatives on the right-hand side of (A 1 b), evaluated at $t = 0$, are readily found from (A 1) and $(2\,d)$. For example, at $t = 0$,

$$\phi' = \tfrac{1}{4}\tan\Phi, \qquad L_\varphi = \sec\Phi, \qquad L_t = -\tfrac{1}{4}(\sec\Phi\tan\Phi + \tfrac{1}{2}\ln\gamma).$$

In this way it can be shown that the series (A 1 a) and (A 1 b) are identical.

If we now substitute (A 1 a) and the formula

$$K = \ln\frac{4}{k'} + \frac{1}{4}\left(\ln\frac{4}{k'} - 1\right)k'^2 + \frac{9}{64}\left(\ln\frac{4}{k'} - \frac{7}{6}\right)k'^4 + \ldots.$$

into (3), we derive

$$\tfrac{1}{4}\kappa R = \ln(4\gamma^{1/2}/k') + (\tfrac{1}{64}k'^4 + \ldots.)\ln k' + \tfrac{1}{2}\ln\Psi(k'^2), \qquad \ldots\ldots(A\,2)$$

where

$$\Psi(k'^2) = \exp\left[-\tfrac{1}{2}k'^2 - \tfrac{1}{64}(13 + 2\ln 4\gamma^{1/2} + \delta)k'^4 + \ldots.\right]. \qquad \ldots\ldots(A\,3)$$

If we now write

$$\chi = \chi_0 \exp\left[(\tfrac{1}{64}k'^4 + \ldots.)\ln k'^2\right], \qquad \ldots\ldots(A\,4)$$

where χ_0 is defined in (12), then (A 2) can be expressed as $k'^2 = \chi\Psi(k'^2)$, where $\Psi(k'^2)$ is an analytic function. Applying Lagrange's theorem, we can invert to derive

$$k'^2 = \sum_{n=1}^{\infty} \frac{\chi^n}{n!}\left[\frac{d^{n-1}}{dx^{n-1}}\Psi^n(x)\right]_{x=0}$$

$$= \chi - \tfrac{1}{2}\chi^2 + \tfrac{1}{64}(11 - 2\ln 4\gamma^{1/2} - \delta)\chi^3 + \ldots.\,. \qquad \ldots\ldots(A\,5)$$

If now (A 4) is approximated by

$$\chi = \chi_0(1 + \tfrac{1}{64}k'^4\ln k'^2 + \ldots.) = \chi_0[1 + \tfrac{1}{64}\chi_0^2(2\ln 4\gamma^{1/2} - \kappa R) + \ldots.],$$

substituting $k'^2 = \chi_0$ into the second term, then (A 5) becomes the required relation (11).

APPENDIX II

We proceed to derive the series (22). Since

$$k=(1+w^2)Z, \quad \sin\phi_0=(Z/k)^{1/2}=(1+w^2)^{-1/2}, \qquad \ldots\ldots(\text{A}\,6a)$$

it follows that

$$\phi_0=\sin^{-1}(1+w^2)^{-1/2}=\int_w^\infty \frac{dw}{(1+w^2)}=\frac{\pi}{2}-w+\frac{w^3}{3}-\frac{w^5}{5}+\ldots\ldots\ldots\ldots(\text{A}\,6b)$$

The expansion of

$$K-F(k,\phi_0)\doteq\int_{\varphi_0}^{\pi/2}\frac{d\phi}{(1-k^2\sin^2\phi)^{1/2}}=G(k,\phi_0), \text{ say},$$

in a Taylor series about $w=0$ is

$$G=G(k,\phi_0)=\frac{w}{(1-Z^2)^{1/2}}\left[1-\frac{1}{3}\frac{(1-\frac{7}{2}Z^2)}{(1-Z^2)}w^2+\frac{1}{5}\frac{(1-\frac{11}{6}Z^2+\frac{149}{24}Z^4)}{(1-Z^2)^2}w^4+\ldots\ldots\right]. \qquad \ldots\ldots(\text{A}\,7)$$

The method used to obtain the result (A 7) is quite simple in principle although rather laborious; it resembles that employed to derive the expansion (A 1). In outlining the derivation of (A 7), we shall again omit the subscript zero on ϕ_0. The quantities k and ϕ are regarded as functions of w, as defined in (A 6*a*). Then k^{i}, k^{ii} and k^{iii} will denote the first three derivatives of k with respect to w (the derivative k^{i} being distinguished from the complement k' of k); ϕ^{i}, ϕ^{ii} and ϕ^{iii} are the corresponding derivatives of ϕ; finally the subscripts k and ϕ on the function G designate partial differentiation. To obtain the first two terms on the right of (A 7), we use the formulae

$$\frac{dG}{dw}=k^{\text{i}}G_k+\phi^{\text{i}}G_\varphi, \qquad \frac{d^2G}{dw^2}=k^{\text{i}2}G_{kk}+k^{\text{ii}}G_k+\phi^{\text{i}2}G_{\varphi\varphi}+\phi^{\text{ii}}G_\varphi+2k^{\text{i}}\phi^{\text{i}}G_{k\varphi},$$

$$\frac{d^3G}{dw^3}=k^{\text{i}3}G_{kkk}+3k^{\text{i}}k^{\text{ii}}G_{kk}+k^{\text{iii}}G_k+\phi^{\text{i}3}G_{\varphi\varphi\varphi}+3\phi^{\text{i}}\phi^{\text{ii}}G_{\varphi\varphi}+\phi^{\text{iii}}G_\varphi$$
$$+3k^{\text{i}2}\phi^{\text{i}}G_{kk\varphi}+3k^{\text{i}}\phi^{\text{i}2}G_{k\varphi\varphi}+3(k^{\text{ii}}\phi^{\text{i}}+k^{\text{i}}\phi^{\text{ii}})G_{k\varphi}.$$

At $w=0$, $\phi=\pi/2$, $G=0$ and all the quantities in the above formulae are zero except $\phi^{\text{i}}=-1$, $\phi^{\text{iii}}=2$, $k^{\text{ii}}=2Z$,

$$G_\varphi=-\frac{1}{(1-Z^2)^{1/2}}, \qquad G_{\varphi\varphi\varphi}=\frac{Z^2}{(1-Z^2)^{3/2}}, \qquad G_{k\varphi}=-\frac{Z}{(1-Z^2)^{3/2}}.$$

The third term in (A 7) can be obtained by considering the higher derivatives of G.

The relation (3) is now expressed in the form

$$\frac{1}{4}\frac{\kappa R}{Z^{1/2}}=S=\frac{w}{(1-Z^2)^{1/2}}\left[1+\frac{1}{6}\frac{(1+4Z^2)}{(1-Z^2)}w^2+\frac{1}{120}\frac{(-11+76Z^2+64Z^4)}{(1-Z^2)^2}w^4+\ldots\ldots\right], \qquad \ldots\ldots(\text{A}\,8)$$

expanding $k^{1/2}$ in powers of w. This is inverted in the usual manner to yield the formula (22).

It is not difficult to obtain the coefficients α_1 and α_3 in (26) by expanding $2F$ in the Taylor series

$$2F=2R\left(\frac{dF}{dR}\right)_{R=0}+\frac{R^3}{3}\left(\frac{d^3F}{dR^3}\right)_{R=0}+\ldots\ldots, \qquad \ldots\ldots(\text{A}\,9)$$

where ψ_0, and hence Z are kept constant when differentiating with respect to R. It is readily seen on examining (10) that the first terms in (A 9) and (26) are identical, since $k \to Z$ as $R \to 0$. From the second relation in (2 b) and from (2 c), we have

$$\cos\phi_0 \frac{d\phi_0}{dk} = -\tfrac{1}{2}k^{-3/2}Z^{1/2}, \qquad -\sin\phi_0\left(\frac{d\phi_0}{dk}\right)^2 + \cos\phi_0 \frac{d^2\phi_0}{dk^2} = \tfrac{3}{4}k^{-5/2}Z^{1/2}.$$

Since $\phi_0 \to \pi/2$ as $R \to 0$, it follows that $d\phi_0/dk \to \infty$ as $1/\cos\phi_0$ and $d^2\phi_0/dk^2 \to \infty$ as $1/\cos^3\phi_0$. Differentiating (3) with respect to k and making use of the above properties,

$$\tfrac{1}{4}\kappa \frac{dR}{dk} k^{-1/2} \to -\frac{\partial F}{\partial \phi_0}\frac{d\phi_0}{dk}, \qquad \tfrac{1}{4}\kappa \frac{d^2R}{dk^2} k^{-1/2} \to -\frac{\partial F}{\partial \phi_0}\frac{d^2\phi_0}{dk^2},$$

as $R \to 0$. Now we derive from (10)

$$2\left(\frac{d^2F}{dR^2}\right)_{R=0} = -nkT\left(\frac{k'^2}{k^2}\frac{dk}{dR}\right)_{R=0} = nkT\frac{(1-Z^2)}{Z^2}\frac{1}{(dR/dk)_{R=0}} = 0,$$

$$2\left(\frac{d^3F}{dR^3}\right)_{R=0} = -nkT\left(\frac{k'^2}{k^2}\frac{d^2k}{dR^2}\right)_{R=0} = nkT\frac{(1-Z^2)}{Z^2}\left[\frac{d^2R/dk^2}{(dR/dk)^3}\right]_{R=0}.$$

Since

$$-\left(\frac{\partial F}{\partial \phi_0}\right)_{R=0} = \frac{1}{(1-Z^2)^{1/2}} \qquad \text{and} \qquad \lim_{R\to 0}\left\{\frac{d^2\phi_0}{dk^2}\Big/\left(\frac{d\phi_0}{dk}\right)^3\right\} = -2Z,$$

it is readily verified that the second term on the right of (A 9) is identical with the second term in (26). The determination of the higher terms by this method is rather involved and consequently will not be attempted here.

Finally, we derive the simplified series (28). When $ve\psi \gg kT$, we may replace $\sinh(ve\psi/kT)$ in (1) by $\frac{1}{2}\exp(ve\psi/kT)$, and Langmuir (1938) has obtained the solution of (1), namely

$$\psi = \psi_m - \frac{2kT}{ve}\ln\cos(\tfrac{1}{2}\kappa x k^{-1/2}). \qquad \text{.....(A 10)}$$

Substituting (A 10) into (6) and replacing $\cosh v\eta_m - 1$ by $\exp(v\eta_m)/2 = 1/2k$, we derive that (5) yields

$$2F = -\frac{4nkT}{\kappa}\frac{4}{\kappa R}u(2\tan u - u)$$

$$= -\frac{4nkT}{\kappa}\frac{4}{\kappa R}u^2(1 + \tfrac{2}{3}u^2 + \tfrac{4}{15}u^4 + \tfrac{34}{315}u^6 + \ldots.), \qquad \text{.....(A 11)}$$

where u is given by (31). Putting $x = R/2$ in (A 10), we obtain the relation

$$u = S\cos u, \qquad \text{.....(A 10 } a\text{)}$$

which can be converted by Lagrange's theorem to yield

$$u = \sum_{n=1}^{\infty}\frac{S^n}{n!}\left[\frac{d^{n-1}}{dx^{n-1}}\cos^n x\right]_{x=0} = S - \tfrac{1}{2}S^3 + \tfrac{13}{24}S^5 - \tfrac{541}{720}S^7 + \ldots. \qquad \text{.....(A 12)}$$

If we now substitute (A 12) into (A 11) and retain only the leading term in the coefficient of each power of S, then it is readily verified that the form (28) is obtained.

APPENDIX III

To obtain (32), we start with the formula

$$\mathrm{dn}\,(u,k)=k'^{1/2}\prod_{n=1}^{\infty}\frac{(1+q^{2n-1}e^{2iv})(1+q^{2n-1}e^{-2iv})}{(1-q^{2n-1}e^{2iv})(1-q^{2n-1}e^{-2iv})}, \qquad \ldots\ldots(\mathrm{A}\,13)$$

where u is defined by (31), $y=(\pi/2K)u$ and $q=\exp(-\pi K'/K)$, the quantity K' being the same function of k' as K is of k (see, for example, Whittaker and Watson, *Modern Analysis*, p. 508). We now expand each term in the infinite series for $\ln \mathrm{dn}\,(u,k)$ in powers of $\exp(\pm 2iy)$, namely

$$\begin{aligned}\ln \mathrm{dn}\,(u,k)&=\tfrac{1}{2}\ln k'+4\sum_{n=1}^{\infty}\sum_{r=0}^{\infty}\frac{q^{(2n-1)(2r+1)}}{(2r+1)}\cos 2y(2r+1)\\&=\tfrac{1}{2}\ln k'+4\sum_{r=0}^{\infty}\frac{q^{2r+1}}{1-q^{2(2r+1)}}\frac{\cos 2y(2r+1)}{(2r+1)}, \qquad \ldots\ldots(\mathrm{A}\,14)\end{aligned}$$

rearranging the resulting double series. If k, K and u are now replaced by k', K' and iu respectively, substitution of (A 14) into (30 a) yields

$$v\eta_0=8\sum_{r=0}^{\infty}\frac{q'^{2r+1}}{1-q'^{2(2r+1)}}\frac{1}{2r+1}\cosh(2r+1)\theta, \qquad \ldots\ldots(\mathrm{A}\,15)$$

where $\qquad q'=\exp(-\pi K/K'), \qquad \theta=\pi\kappa R k^{-1/2}/4K'.$

From the theory of theta-functions

$$q'=\epsilon'+2\epsilon'^{5}+15\epsilon'^{9}+\ldots\ldots,$$

where $$\epsilon'=\tfrac{1}{2}\frac{(1-k^{1/2})}{(1+k^{1/2})}=\tfrac{1}{2}\tanh\tfrac{1}{4}v\eta_{\mathrm{m}},$$

remembering that k' has been substituted for k. Then (A 15) expresses η_0 in terms of η_{m} (and κR).

We shall retain the first three terms in the expansion (A 15), which we write as

$$v\eta_0\simeq 8[\epsilon'(1+\epsilon'^{2}+3\epsilon'^{4})\cosh\theta+\tfrac{1}{3}\epsilon'^{3}\cosh 3\theta+\tfrac{1}{5}\epsilon'^{5}\cosh 5\theta], \qquad \ldots\ldots(\mathrm{A}\,16)$$

neglecting terms of order ϵ'^{7}. Now, if we expand

$$K'=\frac{\pi}{2}\left(1+\tfrac{1}{4}k'^{2}+\frac{9}{64}k'^{4}+\frac{25}{256}k'^{6}+\frac{1225}{(128)^2}k'^{8}+\ldots.\right)$$

and express $k'^{2}=1-\exp(-2v\eta_{\mathrm{m}})$ and $k^{-1/2}=\exp(v\eta_{\mathrm{m}}/2)$ in powers of $v\eta_{\mathrm{m}}$, then

$$\pi k^{-1/2}/2K'=1+f, \qquad f=\tfrac{1}{16}(v\eta_{\mathrm{m}})^{2}\{1+\tfrac{1}{192}(v\eta_{\mathrm{m}})^{2}+\ldots.\}.$$

Writing

$$\begin{aligned}&\cosh\theta\simeq\{1+\tfrac{1}{8}(\kappa Rf)^{2}\}\cosh\tfrac{1}{2}\kappa R+\tfrac{1}{2}\kappa Rf\sinh\tfrac{1}{2}\kappa R,\\&\cosh 3\theta\simeq\cosh\tfrac{3}{2}\kappa R+\tfrac{3}{2}\kappa Rf\sinh\tfrac{3}{2}\kappa R,\\&\cosh 5\theta\simeq\cosh\tfrac{5}{2}\kappa R,\end{aligned}$$

(A 16) can be expressed as

$$\begin{aligned}v\eta_0=v\eta_{\mathrm{m}}&\cosh\tfrac{1}{2}\kappa R+\tfrac{1}{32}(v\eta_{\mathrm{m}})^{3}\sinh\tfrac{1}{2}\kappa R(\kappa R+\tfrac{3}{8}\sinh\tfrac{1}{2}\kappa R\cosh\tfrac{1}{2}\kappa R)\\&+\frac{1}{4(16)^2}(v\eta_{\mathrm{m}})^{5}\{\tfrac{1}{2}(\kappa R)^{2}\cosh\tfrac{1}{2}\kappa R\\&+\tfrac{1}{2}\kappa R\sinh\tfrac{1}{2}\kappa R(4\cosh^{2}\tfrac{1}{2}\kappa R-1)\\&+\tfrac{1}{15}\sinh^{2}\tfrac{1}{2}\kappa R\cosh\tfrac{1}{2}\kappa R(23\cosh^{2}\tfrac{1}{2}\kappa R-12)\}+\ldots. \qquad \ldots\ldots(\mathrm{A}\,17)\end{aligned}$$

which is inverted to yield (32).

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Equations of Motion in General Relativity: II*
The Coordinate Condition

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ABSTRACT. The paper contains a discussion of the necessity for using a coordinate condition in the calculations for the derivation of the equations of motion from the field equations. It is found that no coordinate condition is necessary in the first approximation; i.e. one gets the Newtonian equations of motion if one merely assumes that the gravitational field is weak and quasi-static. In the higher approximations a coordinate condition is indispensable in order to eliminate all apparent accelerations from the equations of motion.

§ 1

As first shown by Einstein and Grommer (1927), the equations of motion of bodies in their own gravitational field can be derived from the field equations alone, without introducing the principle of geodesics as an independent postulate. Later in a series of papers Einstein and co-workers (1938, 1940, 1949) have developed a method for deriving the equations of motion from the field equations in the case of weak fields and slow motions, and they calculated the equations of motion to the second approximation (i.e. up to terms of the second order in v/c). In this method only the field equations for the empty space surrounding the moving bodies are used; because of this feature the method is only applicable to bodies having spherical symmetry. Another method, in which the interior of the moving bodies is also considered and the restriction to spherical symmetry does not apply, has been developed by Fock (1939) and Papapetrou (1951, to be referred to as I).

In all these calculations one has made use of a coordinate condition, which is a set of four differential equations of the first order in $g_{\mu\nu}$. Einstein and co-workers use the following coordinate condition†

$$\gamma_{00,0}-\gamma_{0i,i}=0, \quad \gamma_{ik,k}=0, \qquad \ldots\ldots(1.1)$$

where $\gamma_{\mu\nu}=h_{\mu\nu}-\frac{1}{2}\eta_{\mu\nu}\eta^{\alpha\beta}h_{\alpha\beta}$, $h_{\mu\nu}=g_{\mu\nu}-\eta_{\mu\nu}$.

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† As usual latin indices take the values 1, 2, 3 only, while Greek indices take the values 1, 2, 3 and 0. A comma denotes differentiation, i.e. $f,_\mu=\partial f/\partial x^\mu$

and $\eta_{\mu\nu}$ is the metrical tensor of special relativity ($\eta_{00}=1$, $\eta_{ik}=-\delta_{ik}$, $\eta_{0i}=0$). In the calculations of Fock and Papapetrou the coordinate condition is

$$\mathfrak{g}^{\mu\nu}{}_{,\nu}=0. \qquad \ldots\ldots(1.2)$$

This condition is identical with (1.1) in the first approximation, but it differs from it in the higher approximations.

The coordinate condition has been introduced mainly in order to simplify the calculations needed for the derivation of the equations of motion. The reason is this: Since the field equations are tensor equations, their general solution contains four arbitrary functions, corresponding to an arbitrary transformation of coordinates. Hence we can make the calculations much less difficult if we introduce a suitably chosen coordinate condition, which eliminates this arbitrariness and at the same time simplifies the field equations.

However, there is another much more important reason for the introduction of the coordinate condition. When we discuss the problem of motion of bodies in their gravitational field, we cannot expect that all possible systems of coordinates will be equally useful. We see this immediately if we consider the simplest case of one isolated body (i.e. a body which is very far from any other). If we should allow the use of *any* system of coordinates, we should find the body to perform *any* kind of motion; but we know from Newtonian mechanics and from special relativity that those systems will be especially advantageous in which the isolated body moves with constant velocity. More generally, if we want to discuss the problem of motion in general relativity, we must find a way to avoid the introduction of the apparent gravitational fields due to arbitrary coordinate transformations; in other words, we must, by some means, introduce inertial frames in general relativity.

It must be stressed, however, that these frames do not need to be a straightforward generalization of the inertial frames of special relativity, from which they might differ in important aspects. We mention two possible differences:

(*a*) The necessity for the introduction of the inertial frames has arisen from the discussion of the motions in a nearly isolated system; it is, therefore, possible that in general relativity the inertial frames have a *local* significance only and do not extend over the whole space–time as in special relativity. Such a feature would correspond in some degree to the current interpretation of general relativity as describing the gravitational field by means of a Riemann space, of which $g_{\mu\nu}$ is the metrical tensor.

(*b*) It has been suggested by Rosen (1940) and Papapetrou (1948) that one can interpret general relativity as a theory of gravitation in flat space ($g_{\mu\nu}$ being the gravitational potential only, and not the metrical tensor of space–time). As pointed out by Rosen, in this interpretation the inertial frames of general relativity will resemble the absolute space of Newtonian mechanics rather than the infinite number of equivalent, relatively moving, inertial frames of special relativity. The purpose of these remarks is to show how difficult it will be to give an exact definition of the inertial frames in general relativity.

It has been already suggested (Papapetrou 1951) that the introduction of the inertial frames in general relativity is the main function of the coordinate condition. Whether this is true or not will be discussed in detail in the present paper. We summarize here the results of this discussion.

If we are interested in the equations of motion to the first approximation only, there is no necessity for any coordinate condition. In this approximation we get the Newtonian equations of motion by only requiring that the solution of the field

equations represents a weak and quasi-static field; this is expressed in more detail by the conditions (i) to (iii) in §2. But when we discuss the second and higher approximations, these conditions are not sufficient to determine the equations of motion uniquely. In this case the only way to eliminate apparent gravitational fields from the equations of motion will be by means of a coordinate condition.

The next question arising out of this discussion is the following: What is the 'correct' coordinate condition? In principle one might hope to answer this question by considering to higher approximations the problem of slow motions in weak fields and then comparing the results of the calculations with observation on, for instance, planetary or stellar motions. But probably such a procedure would not be very successful; already one has calculated the equations of motion to the second approximation, but from the consequences of these equations only the secular rotation of the perihelion of a planet could be compared with observation. It seems, therefore, more probable that this question, together with the exact definition of the inertial frames, will be answered by a discussion of more general problems.

§ 2

In addition to the coordinate condition in their calculations Einstein and co-workers as well as Fock and Papapetrou make use of the following three assumptions.

(i) The gravitational field is weak, developable in a power series of a small parameter. According to Fock's suggestion we represent this parameter by the quantity $1/c$. But now we take $x^0 = ct$ (and not, as Fock did, $x^0 = t$). Then we express this assumption by the relation

$$g_{\mu\nu} = \eta_{\mu\nu} + \frac{4}{c} v_{\mu\nu} + \frac{4}{c^2} u_{\mu\nu} + \dots . \qquad \dots\dots(2.1)$$

(ii) The field is slowly changing with time or quasi-static, the derivative $g_{\mu\nu,0}$ being of an order higher by one than the derivative $g_{\mu\nu,i}$:

$$g_{\mu\nu,0} \sim \frac{1}{c} g_{\mu\nu,i} \quad . \qquad \dots\dots(2.2)$$

(iii) The mechanical tensor $T^{\mu\nu}$ starts with the terms familiar in special relativity:

$$\mathfrak{T}^{00} = \rho c^2 + \dots , \quad \mathfrak{T}^{0i} = \rho c v^i + \dots , \quad \mathfrak{T}^{ik} = \rho v^i v^k + p^{ik} + \dots ; \qquad \dots\dots(2.3)$$

ρ is the mass-density, $v^i = dx^i/dt$ the three-dimensional velocity of the mass element and p^{ik} a three-dimensional stress-tensor*; as usual, dots will denote terms of a higher order. It must be stressed that because of (ii) all velocities will be small compared with c:

$$|v^i| \ll c. \qquad \dots\dots(2.4)$$

We shall prove that for the derivation of the equations of motion to the first approximation there is no necessity of any coordinate condition; the conditions (i) to (iii) are already sufficient to lead to the Newtonian equations of motion. We shall give two independent proofs. In the first proof (§ 3) we shall start from the system of coordinates which has been used in the calculations of Einstein and

* The previous calculations of Fock and Papapetrou referred to a perfect fluid, $p^{ik} = p\delta_{ik}$. Here we shall retain the more general form p^{ik}.

co-workers or Fock and Papapetrou; in this system the conditions (i) to (iii) *together* with the coordinate condition (1.1) or (1.2) are fulfilled and the equations of motion have the Newtonian form. We shall then determine the kind of transformation which leads from this system of coordinates to those systems in which only the conditions (i) to (iii) are fulfilled. From the form of these transformations we shall be able to prove, by kinematic considerations, that the equations of motion will not change when we abandon the coordinate condition.

The second proof (§ 4) consists in a direct derivation of the equations of motion from the field equations by using the conditions (i) to (iii) only. Compared with the second proof the first has the advantage that it can also be used for a discussion of the second approximation (see § 5), in which case a direct calculation on the lines of the second proof would be extremely difficult. There is also a third possible proof by using the very elegant method given by Einstein and Infeld (1949). One calculates the additional terms which enter in the expressions for the $g_{\mu\nu}$ when the coordinate condition is dropped; then one shows that these new terms give a vanishing total contribution when introduced in the integral conditions which lead to the equations of motion. Unfortunately the necessary calculations seem to be extremely lengthy, thus reducing the practical value of this method.

§ 3

We shall denote by $x^{*\mu}$ the system of coordinates used in the calculations of either Einstein and co-workers or Fock and Papapetrou. In this system the conditions (i) to (iii) *and* the coordinate condition (1.1) or (1.2) are fulfilled†, and the equations of motion have the Newtonian form; i.e. for spherically symmetrical bodies they are

$$\frac{dv^{*i}}{dt^*} = \frac{\partial}{\partial x^{*i}} \sum_b{}' (m_b^*/r_{ab}^*); \qquad \ldots\ldots(3.1)$$

the indices a, b characterize the bodies of the system, and $\sum_b{}'$ denotes summation over all bodies b except the body a. Then we denote by x^μ any system in which only the conditions (i) to (iii) are fulfilled. The transformation formula connecting x^μ with $x^{*\mu}$ can be written in the form

$$x^{*\mu} = x^\mu + f^\mu(x^\nu). \qquad \ldots\ldots(3.2)$$

If now we make use of the transformation formula for the tensor $g_{\mu\nu}$,

$$g_{\mu\nu} = \frac{\partial x^{*\alpha}}{\partial x^\mu} \frac{\partial x^{*\beta}}{\partial x^\nu} g^*_{\alpha\beta},$$

we easily see that in order that the conditions (i) and (ii) may be fulfilled in the frame x^μ the functions f^μ must be small, of (at least) the first order ‡:

$$f^\mu = \frac{4}{c} a^\mu + \ldots., \qquad \ldots\ldots(3.3)$$

the a^μ being four arbitrary functions of x^i and t whose derivatives $a^\mu{}_{,k}$ and $a^\mu{}_{,4}$ are of the same order.

† We remind the reader that these two coordinate conditions are identical in the first approximation.

‡ We have omitted rotations of the system of coordinates, which are unimportant for our argument.

It is easy to see that as a consequence of (3.3) the condition (iii) is also fulfilled in the frame x^μ. We write (3.2) in the form $x^\mu = x^{*\mu} + f^{*\mu}$ with $f^{*\mu} = -f^\mu$. It follows then from the transformation formula of tensors, because of (3.3), that

$$T^{00} = T^{*00} + \ldots, \qquad T^{0i} = T^{*0i} + \ldots, \qquad T^{ik} = T^{*ik} + \ldots \qquad \ldots\ldots (3.4)$$

On the other hand

$$v^i = \frac{dx^i}{dt} = \frac{dx^{*i}}{dt^*} + \ldots = v^{*i} + \ldots, \qquad \ldots\ldots (3.5)$$

and if we still notice that

$$\sqrt{-g} = 1 + \ldots, \qquad \sqrt{-g^*} = 1 + \ldots,$$

and that (iii) is fulfilled in the frame $x^{*\mu}$, we see that equation (3.4) expresses the validity of (iii) in the frame x^μ. †

From (3.5) and (3.2), (3.3) we also find

$$\frac{dv^i}{dt} = \frac{dv^{*i}}{dt^*} + \ldots.$$

Since, according to (3.2) and (3.3) $r = r^* + \ldots$. and $\frac{\partial f}{\partial x^i} = \frac{\partial f}{\partial x^{*i}} + \ldots$, we can write equation (3.1) in the form

$$\frac{dv^i}{dt} = \frac{\partial}{\partial x^i} \sum_b{}' (m_b^*/r_{ab}) + \ldots. \qquad \ldots\ldots (3.6)$$

The terms of higher order, represented by the dots on the right-hand side of this equation, are unimportant since the initial equation (3.1) is valid only up to terms of this order. Hence equation (3.6) shows that to the first approximation the equations of motion have the Newtonian form in all frames x^μ in which the conditions (i) to (iii) are fulfilled. ‡

It will be interesting to give an example which shows the rôle played by the condition (ii) in eliminating all apparent accelerations from the equations of motion. If (ii) were abandoned, we could satisfy (i) and (iii) by taking in (3.2) $f^i = b^i(t)$, $f^0 = 0$, with b^i of the zeroth order. Then we find from (3.2), since $t = t^*$,

$$v^{*i} = v^i + \frac{db^i}{dt}, \qquad \frac{dv^{*i}}{dt^*} = \frac{dv^i}{dt} + \frac{d^2b^i}{dt^2}.$$

Hence in the frame x^μ the equations of motion will contain the additional terms d^2b^i/dt^2 with *arbitrary* functions b^i; evidently these represent apparent accelerations arising from the use of a non-inertial frame. Thus we see that the condition (ii) is indispensable for the complete definition of the inertial frames. §

† It is worth mentioning that this conclusion holds only for the contravariant components $T^{\mu\nu}$ or $\mathfrak{T}^{\mu\nu}$. We find, for instance, for T_{0i}, $T_{0i} = T^*_{0i} + f^0{}_{,} T^*_{00} + \ldots$, both terms on the right-hand side being of the same order. It is therefore essential that the condition (iii) be written with upper indices.

‡ The fact that the masses of the bodies have the same values in all these frames is again a consequence of the specific features of the transformation (3.2), (3.3). It follows namely from the first of (3.4) $\rho = \rho^* + \ldots$. And since according to (3.2), (3.3) the volume elements are also in the relation $dV = dV^* + \ldots$, it will be $m = m^* + \ldots$.

§ More exactly the conditions (i) to (iii) reduce the apparent accelerations to an order $\leqslant 1/c$. See § 5 where we shall prove that these conditions are not sufficient to determine the equations of motion uniquely in the higher approximations.

§ 4

We shall now prove, by a direct calculation, that the field equations and the conditions (i) to (iii) lead, in the first approximation, to the Newtonian equations of motion. We write the field equations in the form

$$R_{\mu\nu} = -\kappa(T_{\mu\nu} - \tfrac{1}{2}g_{\mu\nu}T) \qquad \ldots\ldots(4.1)$$

with

$$\kappa = 8\pi G/c^4; \qquad \ldots\ldots(4.2)$$

G is Newton's gravitational constant. Using the expression (2.1) for $g_{\mu\nu}$ we see immediately that the quantities $R_{\mu\nu}$ will start with terms of the order $1/c$. We call $R'_{\mu\nu}$ the part of $R_{\mu\nu}$ which is of the order $1/c$, $R''_{\mu\nu}$ the part of the order $1/c^2$ etc.

Thus

$$R_{\mu\nu} = R'_{\mu\nu} + R''_{\mu\nu} + \ldots . \quad .$$

In the right-hand side of (4.1) the quantities $T_{\mu\nu}$ and T start with terms of the order c^2. Hence, because of (4.2), the right-hand side of (4.1) will start with terms of the order $1/c^2$. It follows that

$$R'_{\mu\nu} = 0. \qquad \ldots\ldots(4.3)$$

A well-known calculation gives*

$$R'_{\mu\nu} = \frac{2}{c}\eta^{\alpha\beta}(v_{\mu\nu,\,\alpha\beta} + v_{\alpha\beta,\,\mu\nu} - v_{\alpha\mu,\,\beta\nu} - v_{\alpha\nu,\,\beta\mu}).$$

Introducing this in (4.3) we get $\eta^{\alpha\beta}(v_{\mu\nu,\,\alpha\beta} + v_{\alpha\beta,\,\mu\nu} - v_{\alpha\mu,\,\beta\nu} - v_{\alpha\nu,\,\beta\mu}) = 0$. The general solution of this equation is $v_{\mu\nu} = a_{\mu,\,\nu} + a_{\nu,\,\mu}$ with four arbitrary functions a_μ. But because of (ii) the derivatives $a_{\mu,\,0}$ will be small of the first order, and thus we find

$$v_{00} = 0, \qquad v_{0i} = a_{0,\,i}, \qquad v_{ik} = a_{i,\,k} + a_{k,\,i}. \qquad \ldots\ldots(4.4)$$

The quantities $u_{\mu\nu}$ will be determined by the field equations (4.1) when considered to the order $1/c^2$. But since only some of these quantities will be needed for our calculations, it is more convenient to start with the dynamical equation

$$\mathfrak{T}^{\nu}_{\mu,\,\nu} - \frac{1}{2}\mathfrak{T}^{\nu\varrho}g_{\nu\varrho,\,\mu} = 0, \qquad \ldots\ldots(4.5)$$

from which the equations of motion will follow. We first calculate the leading terms in the expressions of $\mathfrak{T}_\mu{}^\nu$. Using (2.3), (2.1) and (4.4) we find

$$\left.\begin{aligned} \mathfrak{T}_0{}^0 &= \rho c^2 + \ldots, & \mathfrak{T}_i{}^0 &= -\rho c(v^i - 4a_{0,\,i}) + \ldots, \\ \mathfrak{T}_0{}^i &= \rho c v^i + \ldots, & \mathfrak{T}_i{}^k &= -\rho(v^i - 4a_{0,\,i})v^k - p^{ik} + \ldots . \end{aligned}\right\} \qquad \ldots\ldots(4.6)$$

Then we calculate the component $\mu = 0$ of (4.5) considering only the leading terms which are of the order c. We find

$$c\rho_{,\,t} + c(\rho v^i)_{,\,i} = 0, \qquad \ldots\ldots(4.7)$$

which is the same as equation (5.8) in I. We follow the motion of a mass-element which at the time t occupies the volume element δV. This volume will change with time and its derivative is

$$\frac{d}{dt}(\delta V) = \delta V\, v^i{}_{,\,i}. \qquad \ldots\ldots(4.8)$$

* Since we shall make no use of Fock's coordinate condition (1.2), it is not necessary to express the equations in terms of the quantities $\mathfrak{g}^{\mu\nu}$; instead we shall use the quantities $g_{\mu\nu}$ expressed by (2.1).

Hence, if we multiply (4.7) by δV and remember that $\rho_{,t}+\rho_{,i}v^i \equiv d\rho/dt$, we find

$$\frac{d}{dt}(\rho\delta V)=0. \qquad \ldots\ldots(4.9)$$

This relation expresses the conservation of mass in the Newtonian approximation

Now we calculate the component $\mu=i$ of (4.5), again considering its leading terms only, which are of the order c^0. A number of terms cancel because of (4.7), and the result is

$$\frac{d}{dt}(\rho v^i)+\rho v^i v^k{}_{,k}+p^{ik}{}_{,k}=-2\rho u_{00,i}+\rho a_{0,it}.$$

Multiplying by δV and again making use of (4.9), we find the equations of motion to be

$$\rho\frac{dv^i}{dt}+p^{ik}{}_{,k}=\rho(-2u_{00}+4a_{0,t})_{,i}. \qquad \ldots\ldots(4.10)$$

We see that from the quantities $u_{\mu\nu}$ we need to calculate u_{00} only.

The quantity u_{00} will be determined from the component $\mu=\nu=0$ of the field equations (4.1) considered to the order of $1/c^2$. The resulting equation is $R''_{00}=-4\pi G\rho/c^2$. A somewhat tedious but quite elementary calculation making use of (2.1) and (4.4) finally gives $R''_{00}=-2\Delta(u_{00}-2a_{0,t})/c^2$. Thus if we put

$$-2u_{00}+4a_{0,t}=u, \qquad \ldots\ldots(4.11)$$

we find for u the equation

$$\Delta u=-4\pi G\rho; \qquad \ldots\ldots(4.12)$$

i.e. u is the Newtonian gravitational potential of the mass-distribution ρ. Introducing u in (4.10) we find

$$\rho\frac{dv^i}{dt}+p^{ik}{}_{,k}=\rho u_{,i}. \qquad \ldots\ldots(4.13)$$

This result is identical with the equations of motion in the Newtonian theory of gravitation: $\rho u_{,i}$ is the gravitational and $-p^{ik}{}_{,k}$ the 'mechanical' force-density acting on the mass-distribution ρ. Thus we have proved that the field equations together with the conditions (i) to (iii) (but without any coordinate condition) lead, in the first approximation, to the Newtonian equations of motion.†

§ 5

Finally we shall discuss the equations of motion to the second approximation. Using the method of transformation of coordinates described in § 3 we shall prove that the conditions (i) to (iii) alone cannot lead to uniquely determined equations of motion in this approximation. We start from the equations of motion which have been calculated in the frame $x^{*\mu}$ (i.e. with a coordinate condition) to the second approximation. The conditions (i) to (iii) allow transformations

† In addition to the fact that we have abandoned the coordinate condition the present proof is more general than that of I in two other ways; here we have considered an arbitrary distribution of matter (in I spherically symmetrical bodies) and arbitrary elastic properties (in I perfect fluid, $p^{ik}=p\delta_{ik}$).

of the form (3.2) with *arbitrary* functions f^μ of the form (3.3). These transformations will introduce arbitrary additional terms of an order $\leqslant 1/c$† into the velocities v^i and the accelerations dv^i/dt and, therefore, into the equations of motion. Since the initial equations of motion—i.e. those derived from the field equations in the frame $x^{*\mu}$—are now correct up to terms of the order $1/c^2$, we must retain all additional terms up to this order.

We shall show, by a simple example, that it is vain to hope that the additional terms in the equations of motion will, in some way, cancel each other. We consider an isolated body which, according to the equations of motion valid in the frame $x^{*\mu}$, will have constant velocity, $v^{*i}=\text{const.}$, even to the second approximation. Taking for f^μ the quantities $f^i=4a^i(t)/c$, $f^0=0$, we find in the corresponding frame x^μ the velocity

$$v^i=\frac{dx^i}{dt}=\frac{dx^i}{dt^*}=v^{*i}-\frac{4}{c}\frac{da^i}{dt}. \quad \text{Hence} \quad \frac{dv^i}{dt}=-\frac{4}{c}\frac{d^2a^i}{dt^2}.$$

Since the conditions (i) to (iii) allow arbitrary functions $a^i(t)$, we see that in the frame x^μ the body will have an arbitrary acceleration of the order $1/c$. The elimination of these apparent accelerations will be possible only by means of a coordinate condition.

However, the use of the conditions (i) to (iii) weakens the necessity for introducing the coordinate condition in the following sense. In order to eliminate from the equations of motion all apparent accelerations to the second approximation it is sufficient to satisfy the coordinate condition up to terms of the order $1/c^2$ (though for the derivation of these equations we had to consider the field equations up to terms of the order $1/c^4$). This explains why calculations based on the two different coordinate conditions (1.1) and (1.2) do give the same equations of motion to the second approximation: these coordinate conditions differ only by terms of the order $1/c^4$.

This result can be generalized as follows. When, in the terminology of Einstein and co-workers, we want to derive the equations of motion to the order $2l$ (i.e. considering in the field equations all terms up to the order c^{-2l}), we only need to fulfil the coordinate condition up to the order $2l'=2l-2$. This formulation also contains the results of §§ 3 and 4: the first approximation corresponds to $2l=2$, and the coordinate condition must then be fulfilled up to the order $2l'=0$; but this is trivial because of the form (2.1) of $g_{\mu\nu}$, i.e. no coordinate condition is needed in this case.

In contrast to our conclusion, Einstein and Infeld (1949) have given a proof that, in the second approximation, the equations of motion are independent of the coordinate condition. But the case that they discuss is a very special one; they keep the coordinate condition unchanged up to terms of the order $1/c^3$ and they drop it for the higher order terms. A very simple calculation shows that this is equivalent to allowing only transformations of the form

$$x^{*i}=x^i+\frac{4}{c^4}a^i(x^k,t), \qquad x^{*0}=x^0+\frac{4}{c^5}a^0(x^k,t); \qquad \ldots\ldots(5.1)$$

but it is clear from our previous considerations that transformations of this kind will give additional terms of the order $1/c^4$, and thus they cannot change the

† We should start with additional terms of the order of $1/c^3$, if we should extend the rule of taking only odd or only even powers of $1/c$ also for f^μ, i.e. if we should allow only odd powers in f^0 and only even ones in f^i.

equations of motion to the second approximation (which are correct only up to terms of the order $1/c^2$). One sees from our argument that one could change the second of equations (5.1) into $x'^0 = x^0 + 4a^0(x^k, t)/c^3$ without affecting the equations of motion. This agrees with our conclusion that for deriving uniquely determined equations of motion to the second approximation it will be sufficient to fulfil the coordinate condition up to terms of the order of $1/c^2$.

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LETTERS TO THE EDITOR

The Excitation of HCO, C_2 and CH Bands in Flame Spectra

In a recent note Herman, Hornbeck and Laidler (1950) have suggested detailed mechanisms for the production and excitation of HCO, C_2 and CH in acetylene flames.

For HCO they suggest a direct addition of C_2H_2 and O_2, the complex then breaking up to two HCO radicals, the overall reaction being exothermic by about 55 kcal/mole, so that a proportion of the HCO may be formed in the electronically excited state if the initial thermal energy is taken into account. They assume that the HCO* has a fairly long life and the absence of HCO bands in rich mixtures is due to de-activation by collision with C_2, CH and OH. The concentration of C_2 and CH certainly seems to us to be too small to have any important effect, and the OH concentration is no higher in rich mixtures than in weak mixtures. HCO has a small dissociation energy and is likely to be thermally unstable, and so will decompose in hot flames, being favoured in chilled or low-temperature flames. We have found (Gaydon and Wolfhard 1950 b) that in flames in which C_2H_2 is partially replaced by CO the C_2 and CH bands are selectively quenched, while the HCO are not appreciably affected, the result being a relative strengthening of HCO. This agrees with the observation of Herman *et al.* (1950) that the HCO bands are relatively enhanced by cooling a flame with CO_2.

For the production of C_2 and CH radicals Herman *et al.* suggest a peroxide mechanism in which C_2 is ultimately formed from a reaction of C_2H, and CH from decomposition of H–C=C=O, both these final steps being very endothermic (to the extent of about 120 and 75 kcal. respectively). We have in the past considered such reactions, but have always dismissed them for a variety of reasons. For the production of CH we must also remember that CH bands are emitted by flames of atomic hydrogen with acetylene, and from flames of fluorine burning with hydrocarbons (Durie 1950), in both of which reactions oxygen is absent. The suggested reaction for producing C_2 seems much too endothermic, and it may be noted that the light yield for C_2 bands per fuel molecule consumed is not much lower in the relatively cool flame with air than in the hot flame with oxygen (Gaydon and Wolfhard 1950 b); also the relative strength of C_2 compared with CH is greater in the flame with air. The high effective rotational temperature for C_2 (Gaydon and Wolfhard 1950 a) suggests an exothermic rather than an endothermic end reaction.

Herman *et al.* suggest that the excitation of C_2 and CH radicals in the reaction zone results from collision with excited HCO or CO_2. We have produced conclusive evidence (Gaydon and Wolfhard 1950 c) that there is some abnormally high excitation in the inner cones of flames, but we think it is unlikely that it is due to HCO* or CO_2*. The effective excitation temperature is highest for slightly rich mixtures, and under these conditions the HCO bands are absent, and we feel that there is little experimental evidence for the existence of appreciable amounts of HCO* in the reaction zones of hot flames of rich mixtures. Also

an electronically excited HCO radical probably carries only about 125 kcal/mole, whereas we have shown that the excitation processes which occur in flames give evidence of at least 173 kcal. being set free. The excited CO_2 molecule might contain sufficient energy, but it is unlikely that CO_2 is formed in the reaction zones of flames of very rich mixtures, and if CO_2^* were responsible it would be difficult to account for the marked quenching of C_2 and CH bands on partial replacement of C_2H_2 with CO. Also, the carbon monoxide flame itself, in which CO_2^* is formed, does not show the high electronic excitation temperatures as measured by the spectrum-line reversal method using Fe, Pb, etc. that hydrocarbon flames show.

Reaction processes in flames are very complex, and the mechanism of formation and excitation of C_2 and CH is probably far from simple, as shown by our replacement experiments (Gaydon and Wolfhard 1950 b), and we have not found any detailed simple reactions which will stand up to criticism. We at present take the view that the initial step is the formation of some active radical, such as either an alkyl radical or perhaps C_2H. This may be formed either by a peroxide mechanism, as suggested by Herman *et al.*, or by stripping hydrogen by atomic hydrogen, fluorine, etc. This is followed by rapid build-up of a more complex molecule (i.e. a form of polymerization), probably of very unsaturated character. Subsequent breaking-up or reaction of this complex molecule is sufficiently exothermic to throw out C_2 or CH radicals. We are not sure whether the C_2 and CH emission is due to chemiluminescence resulting from this breaking-up, but we think it more likely that the excitation is a subsequent process resulting from the presence of some unknown active species in the flame gases.

Chemical Engineering Dept.,
Imperial College, London S.W.7.
7th December 1950.

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Positron Electron Branching

We have determined the $\beta^+ : \beta^-$ branching ratio of ^{80}Br by observing the γ–γ coincidences due to annihilation quanta. Eight other isotopes were investigated for possible positron branching by the same method and gave negative results.

All sources were mounted in polystyrene. Two photomultiplier tubes (E.M.I. 1 in. aperture type with naphthalene anthracene crystals) were placed in coincidence (resolving time $1{\cdot}5 \times 10^{-7}$ sec.) and on opposite sides of the source at 65 cm. distance to detect the annihilation γ-rays. With this small solid angle (10^{-4} of 4π) the probability of observing a coincidence due to a nuclear γ-ray cascade is of the order of 10^{-4} smaller than the probability of detecting a positron. Coincidences due to annihilation are easily distinguished from all others; if the source is displaced by 2·5 cm. out of the straight line joining the two detectors, they disappear. Frequent comparisons were made with a ^{22}Na standard (calibrated by its γ-ray against ^{60}Co (Mims, Halban and Wilson 1950)).

A quantity of NH_4Br was irradiated for 5 hours in the Harwell pile; decay measurements showed that 90% of the activity was due to ^{80}Br (4·5 hr.) and 10% to ^{82}Br (35 hr.). A sample was compared by absolute β counting with a ^{24}Na source calibrated by the β–γ coincidence method. The correction for differences in adsorption of the β-rays was small (1%). Scattering was minimized by mounting the sources on thin Styrafoil and by placing diaphragms between source and counter. Since both ^{80}Br and ^{24}Na sources were prepared and counted under the same conditions it was assumed that scattering contributions did not differ significantly.

Annihilation counts were observed to fall off with a half-life of 4·58 hours; this seems in good agreement with the period for the isomeric level feeding the ground state of ^{80}Br. A positron : electron ratio of 1 : 27 was found (compared with 1 : 35 obtained by Barber (1947)). Reynolds (1950) gives $0{\cdot}09 \pm 0{\cdot}002$ for the ratio K capture $+ \beta^+ : \beta^-$, which, combined with our results leads to $(1{\cdot}43 \pm 0{\cdot}17) : 1$ for the ratio K capture to β^+.

Eight other isotopes were examined for positron emission, a calibrated γ-ray counter being used to standardize the sources; a precision of 10% is easily obtained.

In ^{110}Ag the observed ratio of $4{\cdot}8 \pm 1 \times 10^{-4}$ positrons per disintegration was explained by pair production due to hard γ-rays. The source of ^{110}Ag was surrounded by lead discs in an experiment to determine the magnitude of this effect. A ratio of 5×10^{-4} in ^{76}As may be similarly explained. The remainder showed no positron emission.

In the list of results given, the standard deviation of the background $\times\sqrt{2}$, i.e. the standard deviation of the difference between on and off line counts, is expressed as an upper limit to the positron branching ratio. Since the positron counting efficiency is independent of positron energy, and since (beyond a relatively small displacement of the source) the conditions of measurement are not changed in order to distinguish annihilation coincidences from background, it is unlikely that a branching process could have been obscured by systematic errors. The odds against a random error greater than standard deviation are 2·2 : 1, against a random error greater than twice standard deviation 21 : 1 etc. In his work with a trochoidal magnetic spectrometer Barber (1947) names 4 times the standard deviation of the background as a safe upper limit.

Our results are as follows: ^{46}Sc$< 1{\cdot}6 \times 10^{-5}$, ^{76}As $6{\cdot}8 \pm 3 \times 10^{-4}$, ^{82}Br$< 2 \times 10^{-4}$, ^{86}Rb$< 1{\cdot}6 \times 10^{-5}$, ^{110}Ag $4{\cdot}8 \times \pm 1 \times 10^{-4}$, ^{134}Cs$< 8{\cdot}6 \times 10^{-5}$, ^{192}Ir$< 8 \times 10^{-5}$, ^{198}Au$< 3{\cdot}3 \times 10^{-5}$. In the cases of ^{76}As and ^{110}Ag the observed effects were attributed to pair production by γ-rays.

To illustrate the inferences which may be made from these data we consider ^{86}Rb. 80% of the β^- transitions occur to the ground state of ^{86}Sr; β^+ decay would lead to ^{86}Kr. Both these end products being even–even nuclei can be expected to have zero spin in their ground state. Supposing then that the β^+ transition, if existing, is allowed or forbidden to the same degree as the β^- transition, a branching ratio of less than 1 in 50,000 implies that less than 0·25 MeV. of kinetic energy is available for the emission of the positron. This is interesting in view of the fact that β^+ decay would lead to a closed shell of 50 neutrons.

Although the other nuclei examined were also of the odd–odd type, an exactly similar argument cannot be applied. Where β^- decay directly to the ground state is highly forbidden so that the transitions occur by means of β- and γ-rays in cascade, β^+ branching might be expected to occur, if at all, in a similar way, i.e. to an excited level of the $Z-1$ nucleus. The lack of branching may be explained by the absence of such a level, and not merely by a small total energy of transition.

The authors wish to thank Lord Cherwell for putting at their disposal the facilities of this laboratory and for his continued interest in the experiments.

Clarendon Laboratory, Oxford.
19th December 1950.

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H. Halban.

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Detection of ^{14}N(γ, d 3α) and ^{14}N(γ, pn 3α) Reactions in Nuclear Emulsions

The identification of 3-particle ^{14}N(γ, 2α)^{6}Li stars, produced in nuclear emulsions by 23 to 25 MeV. bremsstrahlung, has already been reported (Wilkins and Goward 1950a) and the possibility of detecting the reaction

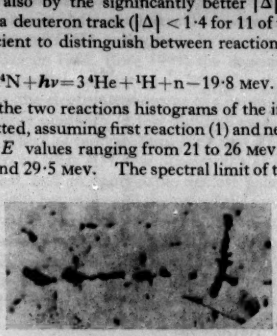
$$^{14}\mathrm{N} + h\nu = 3\,^{4}\mathrm{He} + {}^{2}\mathrm{H} - 17{\cdot}6 \text{ MeV.} \qquad \ldots\ldots (1)$$

was mentioned. This reaction might be expected since 4-particle nitrogen stars have been observed in a cloud chamber (Gaerttner and Yeater 1950). Stars from the reaction have now been identified with certainty in emulsions exposed to 25·5 MeV. bremsstrahlung; a typical example is shown in the Figure. The identity of the stars may be established by an argument very similar to that used in identifying the 3-particle stars.

If a histogram is plotted of the apparent momentum balance, $|\Delta|$ in (mass number × Mev.)[13] units, for 233 observed 4-particle stars, assuming them to be $^{16}O(\gamma, 4\alpha)$ stars, 25 have $|\Delta$ values in excess of 1·4. Of these, 13 are identifiable as nitrogen disintegrations by the fact that they include one reasonably long ($>15\,\mu$) track of appreciably reduced grain density, and also by the significantly better $|\Delta|$ values obtained when the light track is assumed to be a deuteron track ($|\Delta| < 1{\cdot}4$ for 11 of the events). This evidence alone, however, is not sufficient to distinguish between reaction (1) and the possible alternative reaction

$$^{14}N + h\nu = 3\,^4He + {}^1H + n - 19{\cdot}8 \text{ Mev.} \quad \ldots\ldots (2)$$

To distinguish between the two reactions histograms of the incident quantum energy E_γ for each selected star are plotted, assuming first reaction (1) and next reaction (2). Assuming reaction (1) the 13 stars give E values ranging from 21 to 26 Mev., but assuming reaction (2) the values lie between 24·5 and 29·5 Mev. The spectral limit of the gamma-rays is 25·5 Mev.



$^{14}N(\gamma, d\,3\alpha)$ star.
Observer: Mrs. J. M. Taylor.

Thus, even allowing for the fact that the neutron energy is determined from $|\Delta|$ in reaction (2) events and will in general be overestimated, the majority of the stars appear to be due to reaction (1) rather than (2). This might perhaps be expected using energies so near the threshold. The cross section is of the order of a few times 10^{-29} cm² at 23 Mev. This cross section, in common with others similarly determined, is subject to spectrum shape and range–energy relationship uncertainties which will be resolved in future publications.

Of the 13 events described, eight have been shown to involve intermediate ground state ^8Be nuclei, using techniques already described (Goward and Wilkins 1950). The difficulties generally met in identifying stars involving these nuclei (Wilkins and Goward 1950 b) are well illustrated by the present investigation: several apparent 3-particle stars observed, with one light track, are almost certainly nitrogen 4-particle stars with one undetectably short track. Allowing for these events, the cross section would be of the order of 10^{-28} cm² at 23 Mev.

Atomic Energy Research Establishment,
Harwell, Didcot, Berks.
21st December 1950.

F. K. Goward.
J. J. Wilkins.

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Alpha-Particles from the Proton Bombardment of Phosphorus

Short range alpha-particles from the reaction $^{31}P(p\alpha)^{28}Si$ have been detected with the aid of a 60° magnetic analyser (constructed in this Laboratory by R. M. Littauer). The particles were observed at an angle of 120° with the direction of the incident protons, and were detected by a thin zinc sulphide screen and an E.M.I. photomultiplier.

Protons of energies 600 to 1,100 kev. from the Cavendish high tension accelerator were used. The voltage scale was calibrated by observations of the thick target gamma-ray excitation function for the $^{19}F(p\alpha, \gamma)^{16}O$ reaction, the resonance values of 873·5, 935 and 1,176 kev. given by Chao *et al.* (1950) being used.

For the current–energy calibration of the magnetic analyser, observations were made on the positions of the peaks of particle groups of known energy, use being made of the

reactions $^{9}Be(pd)^{8}Be$ and $^{9}Be(p\alpha)^{6}Li$ ($Q=0{\cdot}558\pm0{\cdot}003$ MeV. and $2{\cdot}121\pm0{\cdot}012$ MeV. respectively, from Tollestrup *et al.* (1949)), $^{19}F(p\alpha)^{16}O^{*}$ ($Q=1{\cdot}978\pm0{\cdot}008$ MeV., from Chao *et al.* (1950) and Freeman (1950 b)), and $^{23}Na(p\alpha)^{20}Ne$ ($Q=2{\cdot}35\pm0{\cdot}04$ MeV., from Freeman (1950 a)). The present result depends chiefly on the ^{19}F calibration points.

The ^{31}P targets were made by evaporating thin layers of zinc phosphide (< 10 kev. for protons) on copper buttons *in vacuo*. The alpha-particle group observed when a phosphorus target was bombarded with protons of energy E =1,025 kev. energy is shown in Figure 1;

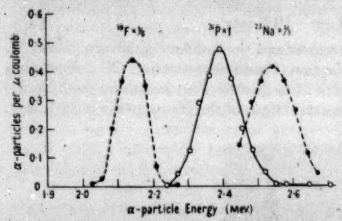

Figure 1. Alpha-particle groups from $^{31}P(p\alpha)^{28}Si$ (E_p=1,025 kev.) and from $^{19}F(p\alpha)^{16}O^{*}$ and $^{23}Na(p\alpha)^{20}Ne$ (E_p=935 and 930 kev. respectively).

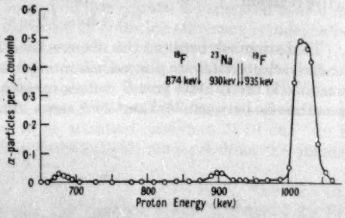

Figure 2. Excitation function for the reaction $^{31}P(p\alpha)^{28}Si$.

alpha-particles obtained by bombarding ^{19}F and ^{23}Na targets with protons of energies 935 and 930 kev. respectively are also shown for comparison. The intensity of the alpha-particle group from the phosphorus reaction was studied as a function of the bombarding voltage for proton energies from 650 to 1,070 kev. The excitation function, which is given in Figure 2, indicates resonances at 680, 900 and 1,025 kev. For comparison the positions of the resonances observed for the ^{19}F and $^{23}Na(p\alpha)$ reactions are shown by arrows.

The width of the peaks shown in Figure 2 is approximately 30 kev., and as this is about equal to the energy spread in the bombarding proton beam the true widths of the resonance levels must be considerably smaller, as would be expected.

The energy release in the $^{31}P(p\alpha)^{28}Si$ reaction was calculated from the energy of the alpha-particle group measured at each of the three resonances. The results are tabulated below:

Proton energy at resonance (kev.)	1025 ± 7	900 ± 5	680 ± 15
Alpha-particle energy (MeV.)	$2{\cdot}393\pm0{\cdot}018$	$2{\cdot}264\pm0{\cdot}029$	$2{\cdot}122\pm0{\cdot}034$
Q (MeV.)	$1{\cdot}860\pm0{\cdot}022$	$1{\cdot}822\pm0{\cdot}034$	$1{\cdot}855\pm0{\cdot}042$
		Weighted mean $Q=1{\cdot}85\pm0{\cdot}02$ MeV.	

In estimating the probable errors, small effects due to target thickness and carbon contamination were taken into account.

The Q-value of $1{\cdot}85\pm0{\cdot}02$ MeV. can be compared with the results recently published by Endt, Van Patter and Buechner (1950) for the reactions $^{31}P(d\alpha)^{29}Si$ and $^{28}Si(dp)^{29}Si$. There the preliminary Q-values for the ground state transitions are given as $8{\cdot}170\pm0{\cdot}020$ and $6{\cdot}246\pm0{\cdot}010$ MeV. respectively; these would lead to a value for the energy release in $^{31}P(p\alpha)^{28}Si$ of $1{\cdot}824\pm0{\cdot}022$ MeV., which is in agreement, within the quoted errors, with our value. These results provide a considerably more accurate figure for the mass difference between ^{31}P and ^{28}Si than has hitherto been available.

One of us (J.S.) is indebted to the Department of Scientific and Industrial Research for a grant.

Cavendish Laboratory,
Cambridge.
19th December 1950.

JOAN M. FREEMAN.
J. SEED.

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On the Spatial Alignment of Nuclei

Interest in the production of polarized nuclei for the investigation of nuclear forces has led to two suggestions for using the interaction between the electron shells and the nucleus to this end. One of these involves the magnetic interaction, the other the electrostatic interaction with the nuclear quadrupole moment.

In the former method (Gorter 1948, Rose 1949) the degeneracy of the nuclear energy levels corresponding to their spatial orientation is lifted by the enormous magnetic field (10^5 to 10^6 gauss) produced by the electronic moment of a paramagnetic ion. If a small field is applied to align the electronic moments (a few hundred gauss is assumed to suffice), the nuclei will also be aligned. Then, at temperatures such that kT is small compared with the width of the hyperfine structure (that is, a few hundredths of a degree) only a few of the nuclear levels will be occupied, and an appreciable nuclear polarization will be set up.

More recently, Pound (1949) has proposed the use of the electric quadrupole interaction to obtain a rather different type of alignment. With a nucleus of spin 3/2, for example, this interaction splits up the four-fold nuclear level into two doublets, with magnetic quantum numbers $m=\pm 3/2$ and $\pm 1/2$ respectively. At very low temperatures, therefore, there will be a preponderance of nuclei in one of these doublets. The ambiguity in sign is no disadvantage in radioactive emission, which is expected to involve even powers of $\cos\theta$ (Spiers 1948, 1949).

The purpose of this note is to point out that in certain cases alignment of the type envisaged by Pound can be obtained by demagnetizing a paramagnetic salt, with hyperfine structure due to magnetic interaction, to zero magnetic field. This simplifies the experimental procedure, and enables lower temperatures to be reached than in Gorter's method. The method suggested depends on the fact that in a number of salts investigated by paramagnetic resonance, the hyperfine structure is found to be exceedingly anisotropic. In copper and cobalt salts (Bleaney 1950) the ratio of the constants A, B of the interaction Hamiltonian

$$AS_zI_z+B(S_xI_x+S_yI_y) \qquad \ldots\ldots (1)$$

may be as much as 6 : 1 or 8 : 1. The nature of the energy level diagram in zero magnetic field may best be seen by neglecting the term in B, when we have, for an effective electronic spin of 1/2, $(2I+1)$ doublets equally spaced by $A/2$ in energy. Each doublet is an equal admixture of the nuclear states $\pm m$, and the order of the doublets is a linear progression $m=\pm I, \pm(I-1), \ldots, \mp I$. Thus at a temperature T, the fraction of the nuclei in the state $\pm m$ is simply proportional to $\cosh(mA/2kT)$. For a spin of 3/2 the ratio of nuclei in the states $\pm 3/2 : \pm 1/2$ is 1·51 : 1 at $kT=3A/4$; in the copper tutton salts this temperature would be about 0·014° K.

As in Pound's method, a single crystal or a number of aligned single crystals are required. Though the hyperfine structure is more complex than in the electric quadrupole case, suitable substances are already at hand whose splittings are considerably greater than any yet detected in the solid state due to quadrupole interaction (Dehmelt and Kruger 1950, Dehmelt 1950). Ideally a crystal with only one ion in unit cell is required, since the axis about which the nuclei process (which is determined by the crystallographic structure) is then parallel for all ions. This condition is nearly fulfilled by cobalt sulphate, diluted with zinc sulphate (Bleaney and Ingram 1951), which has four ions in unit cell, with their axes only 13° from the crystallographic c-axis. For this salt $A=0{\cdot}035°$, while B is only 0·004°, for the stable isotope ^{59}Co; for a radioactive isotope they would be scaled in proportion to the nuclear gyromagnetic ratios. It should be noted that diluted crystals would be required, since otherwise the alignment would be spoiled by the magnetic fields of neighbouring ions. These are of the same order as the field exerted on the electron shell of an ion by its own nucleus. The degree of dilution required can be adjudged by the criterion that the hyperfine structure should be reasonably well resolved in a paramagnetic resonance experiment.

Several alternatives present themselves for the cooling of the salt: (*a*) it may be maintained in thermal contact (e.g. by using a mixed crystal) with another paramagnetic salt, which is cooled by adiabatic demagnetization; (*b*) if the radioactive isotope is of an element whose stable isotopes have no nuclear moment, demagnetization of the latter will produce very efficient cooling; (*c*) a certain degree of alignment can be produced even if the stable

isotopes of the element have a hyperfine structure comparable with that of the radioactive isotope. For example, at the lowest temperature which could be reached by demagnetization of diluted cobalt sulphate the numbers of the ^{59}Co nuclei in the states $\pm 7/2 : \pm 5/2 : \pm 3/2 : \pm 1/2$ would be in the ratio $1 : 0{\cdot}53 : 0{\cdot}32 : 0{\cdot}21$.

If the value of B is not negligible, the quantization is somewhat spoiled because the state with nuclear magnetic quantum number m has admixed with it the states $m \pm 1$ to an extent of the order $(B/A)^2$. This is more serious with isotopes of low spin than of high spin. If $B=A$, the levels fall into two groups corresponding to the usual resultant quantum number F, with values $I+\frac{1}{2}$ and $I-\frac{1}{2}$. The nuclear orientations are then very intermixed and no alignment is set up in zero field. An exception to this is where there is a large splitting of the electronic levels due to the crystalline field, with the states $\pm S$ at the bottom. Then the off-diagonal elements due to the term in B in (1) are again negligible, and we have a similar situation to that of high anisotropy.

It is interesting to note that the requirements of the method suggested above give also the most favourable conditions in Gorter's method since then a first order Zeeman effect is produced by a small field parallel to the crystalline symmetry axis. Under other conditions only a second order effect exists until fields are applied large enough to overcome the orientation around the crystal axes due to the hyperfine structure or the crystalline splittings.

These questions of the production of nuclear alignment by hyperfine structure in paramagnetic salts will be considered more fully in a forthcoming paper. It is hoped also shortly to undertake experiments on the lines indicated in this letter using the radioactive isotope, ^{60}Co.

Clarendon Laboratory, B. Bleaney.
Oxford.
29th December 1950.

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Note on the Adiabatic Demagnetization of Cobalt Ammonium Sulphate

Recently Garrett (1950) has reported measurements of the magnetic properties of cobalt ammonium sulphate below $0{\cdot}1°$ K., and the anomalous behaviour in this region is attributed to an order–disorder transition. It seems that no account has been taken of the hyperfine splitting in this salt, which would also give rise to anomalous behaviour in this temperature region. The purpose of this note is to give an estimate of these effects, which can be calculated from the data provided by paramagnetic resonance experiments.

The behaviour of the spin levels can be represented by the Hamiltonian

$$\mathcal{H} = \beta\{g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)\} + AS_zI_z + B(S_xI_x + S_yI_y) - \gamma\beta_N HI, \quad \ldots\ldots (1)$$

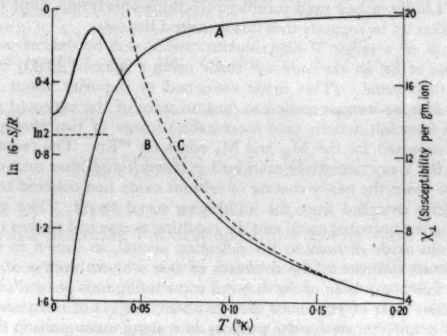
where $S=1/2$, $I=7/2$; $g_{\parallel}=6{\cdot}45$, $g_{\perp}=3{\cdot}02$; $A=0{\cdot}0344°$ K., $B=0{\cdot}0029°$ K. (Bleaney and Ingram 1949, 1951). As the value of B is so small compared with A, it may be neglected in a first approximation. The energy levels in zero magnetic field consist then of seven equally spaced doublets, with an overall separation of $7A/2=0{\cdot}120°$ K. The entropy drop associated with this splitting can be calculated using the tables of Giauque, Stout, Egan and Clark (1941) for the entropy of magnetization of an ion of spin 7/2 by equating their variable x to $7A/4T$. The steep drop below $0{\cdot}1°$ K. is shown in the Figure.

The effect of the hyperfine splitting on the susceptibility is rather interesting. If a magnetic field is applied along the z-direction (the tetragonal axis of the cobalt ion) each doublet is split by a first-order Zeeman effect of the same amount. The susceptibility

therefore follows Curie's law, irrespective of the changing population of the different doublets. If the magnetic field is applied perpendicular to the axis, only a second-order Zeeman effect is produced. The value of $\chi_\perp$ is given by the expression

$$\chi_\perp = \frac{Ng_\perp^2\beta^2}{kA}\left\{\frac{\Sigma_m (1/2m)\sinh(mA/2kT)}{\Sigma_m \cosh(mA/2kT)}\right\}, \qquad \ldots\ldots (2)$$

where m takes the values $\frac{1}{2}, \frac{3}{2}, \ldots, I-1, I$, while $\chi_\parallel = Ng_\parallel^2\beta^2/4kT$. The molar susceptibility perpendicular to the axis is shown in the Figure; it passes through a maximum at 0·024° K. and then falls to a constant value. Down to 0·05° K. the susceptibility in any



Dilute cobalt ammonium sulphate below 0·2° K.

Curve A : Entropy, $\ln 16 - S/R$.

Curve B : Susceptibility normal to tetragonal axis, showing anomaly due to hyperfine structure.

Curve C : Susceptibility normal to tetragonal axis, in absence of hyperfine structure.

direction can be written to a good approximation as $\chi=(C/T)\{1-(\tau/T)^2\}$ and the values of C and τ are given in the Table for the principal axes of the crystal and of each ion (K_2 is perpendicular to the tetragonal axis) and for a powder.

Axis	Tetragonal	K_1	K_2	K_3	Powder
C (per mole)	3·90	3·00	0·86	1·75	1·87
τ (° K.)	0	0·007	0·023	0·014	0·013

These expressions for the susceptibility apply only to a very dilute salt, since no correction has been made for dipole–dipole interaction. The deviations from Curie's law are small, though not negligible, in the temperature region of Garrett's anomaly, which is observed in the concentrated salt. Thus, though the effect of the hyperfine structure must be included in any complete theory, Garrett's anomaly must be attributed in the main to some other cause.

The contribution to the susceptibility from the nuclear moment is negligible. For fields along the axis, the latter causes a slight change in the effective value of g, positive for some levels, negative for others. Perpendicular to the axis the nuclear susceptibility becomes temperature independent, in the same region as the electronic susceptibility, and thus can never be important.

The results outlined in this note form part of a more detailed examination of the effects of hyperfine structure in paramagnetic salts, which will be published shortly.

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Clarendon Laboratory,
Oxford.
29th December 1950.

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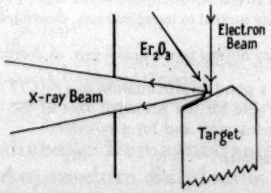
The M_{IV} and M_V Absorption Edges of ^{68}Er

X-ray absorption in the $M_{IV,V}$ region by ^{68}Er has been observed hitherto only by Lindberg (1931) who, however, failed to observe any sign of the normal M_{IV} and M_V edges but found instead a pair of narrow absorption lines close to the expected position of the M_V edge. The wavelengths of these lines he gives as 8822 X.U. and 8805 X.U. He obtained a similar remarkable result for ^{70}Yb—in this case a single sharp absorption line at 8138 X.U., again close to the expected M_V edge. The Yb result has been confirmed in this laboratory (Stewardson and Zandy 1950) for absorbing films up to a thickness of 0·13 mg. of Yb_2O_3 per cm^2. On the other hand, as a result of a careful study of the variation in the structure of the M_{IV} and M_V edges of ^{62}Sm with thickness of the absorbing layer, Rule (1945) suggested that Lindberg had used insufficiently thick absorption films of Er and Yb. A chance observation by us suggests that this is indeed the case.

In the course of a series of experiments carried out by one of us (P.A.L.) on the M-emission lines of Er, an exposure was made using a layer of Er_2O_3 on the anticathode much heavier than usual. (This oxide contained as impurity about 15% Y_2O_3.) On developing the film we were surprised to find no trace of the expected emission lines but found instead a faint but definite (and measurable) image of two absorption edges at the positions to be expected for the M_{IV} and M_V edges for ^{68}Er. The reason for this became apparent when the X-ray target was examined. It was found that under the action of the focused electron beam the heavy coating of erbium oxide had cohered together, curled up and become partly detached from the underlying metal target. The electron beam was therefore striking the uncoated metal and the resulting X-rays had to pass through the curled up film of erbium oxide *en route* to the reflecting crystal, as shown in the accompanying diagram. An exact estimate of the thickness of this erbium layer is of course out of the question, but it must have been of the order of some milligrams per cm^2, i.e. about 10 times that of the thickest layer of ytterbium used to obtain the result mentioned by Stewardson and Zandy. It is unfortunate for the purpose of making a comparison that Lindberg does not mention the thickness of the erbium absorption films he used. By great good fortune



on the same film as that on which the edges appeared there were registered faintly also the $K\alpha_1$ and $K\beta_1$ lines of ^{25}Mn in the fifth and fourth orders respectively and using these as reference lines the wavelengths of the erbium edges have been determined. The resulting values are : M_{IV} edge, 8583 X.U.; M_V edge, 8829 X.U. As these values are obtained from a rather faint image on a single negative the fourth figure is certainly not reliable, but we would estimate the possible error as being not in excess of ± 10 X.U. (the dispersion of the spectrograph was of the order of 40 X.U. per mm.). There was no sign of any fine structure at the edges but it is unlikely that any structure would be visible on such a thin negative. Certainly Lindberg's results for an apparently much thinner absorption film suggest that some fine structure may exist at the M_V edge. It is remarkable however that both his lines lie on the *high-frequency* side of the edge as measured by us, the difference in one case being greater than would seem likely to be accounted for by experimental error alone, but of this we cannot be certain at this stage. It is hoped soon to make a series of observations using a wide range of thicknesses of absorption films of Er to clear up this point.

The wavelengths of the edges found from this photograph make it possible to estimate the L–M discrepancy for Er. Using the values for $L\alpha_1$, $L\alpha_2$, and $L\beta_1$ for erbium given by Wennerlöf (1930) and for the L_{II} and L_{III} edges by Eddy (1925) we find the following values for the discrepancies :

$$M_{IV}(\text{meas.}) - M_{IV}(\text{calc.}) = -1{\cdot}11(\nu/R) = -15{\cdot}1 \text{ ev.}$$
$$M_V(\text{meas.}) - M_V(\text{calc.}) = -1{\cdot}10(\nu/R) = -14{\cdot}9 \text{ ev.}$$

These values appear larger than one would expect, and although this may be due to uncertainties in our measurements it would seem nevertheless that the discrepancies are definitely negative and probably of the same order of magnitude as those found in the case of other rare earth elements by Stewardson and Zandy.

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2nd January 1951.

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REVIEWS OF BOOKS

Counting Tubes, by S. C. CURRAN and J. D. CRAGGS. Pp. xi+238. (London: Butterworth's Scientific Publications Ltd. 1949.) 35*s*.

Books on ion counters are few and far between. There is still an urgent need for a comprehensive and up-to-date treatment of the subject. The present book deals almost exclusively with the gas-filled type of counter, with the exception of one chapter which gives a brief discussion of some other types such as scintillation and crystal counters. The early part of the book summarizes the relevant background information on electrical discharges and of the ionization produced by fast particles, and then goes on to analyse the behaviour of counting tubes in the different voltage regimes. There follow three chapters which deal with the efficiency of counters, their construction, and some of the auxiliary circuits to be used with them. The remainder of the book comprises the chapter on special types of counter already mentioned and some chapters dealing with representative applications of counter tubes in different fields of research.

The authors have included a great deal of useful information on the different phenomena which occur in counter tubes and there is a good selection of references to the original literature. The book was, however, found to be a difficult one to read. This was due in part to insufficient care in the definition of terms and symbols in a number of places and, in part, to an over-condensed treatment of the material. In fact—rightly or wrongly—the impression was gained that the book had been written rather hurriedly. Nor, unfortunately, is the text free from error. In the section dealing with the resolving power of counters, the argument leading to equation (40) on page 95 is definitely fallacious and it is not correct for the authors to state, as they do on the following page, that it is difficult to decide whether this or equation (42) is the more nearly correct. Certainly confusion has existed on this point in the past, but it has now been clarified and the matter is adequately dealt with in the literature.

The authors state in their preface that they hope that " this book will appeal both to graduates about to commence experimental work and to undergraduate students who find it necessary to use Geiger counters as instruments. In other fields such as medicine and chemistry an increasing number of workers are finding it necessary to use counters in their researches and we hope that this book will be of assistance to them, if only as a source book ". It is felt that the potential value of the book has been diminished by trying to cast the net too wide. Those whose interest is primarily in the use of the counter as a tool are liable to find their understanding of the broad principles of its behaviour obscured by a fog of detail concerning little-understood processes in the discharge, while to those for whom these details are of importance, the chapters dealing with sundry applications of counter tubes are likely to be redundant. It is to be hoped that the authors will find it possible to remedy these defects in a second edition.

J. L. M.

Theoretical Hydrodynamics, by L. M. MILNE-THOMSON. Pp. xxi + 600. 2nd Edition. (London: Macmillan and Co. Ltd., 1949.) 60*s*.

The best way to regard this book appears to be as a textbook primarily concerned with the applications of vector methods, and of the theory of functions of a complex variable, to certain of the less difficult parts of hydrodynamical theory. It is concerned, in particular, with potential motions of ideal, incompressible fluids, and with the calculations of such motions past or along solid boundaries of a ' simple ' geometrical shape. Judged in this way, the book is good and satisfactory.

No less than eleven chapters out of twenty, occupying more than half the book, deal with two-dimensional motion and the complex variable, including chapters on the complex variable itself, on aerofoils, on the Schwarz–Christoffel conformal mapping of the interior of a polygon and its applications to jets, currents and wakes, on rectilinear vortices, and on two-dimensional wave motion. There is an introductory chapter, mainly on Bernoulli's equation and some of its consequences, a chapter on vectors, two on three-dimensional potential motions (one on axisymmetrical motion (Stokes's stream function) and one on potential motions with spherical and ellipsoidal boundaries), and one chapter each on the dynamical theory of the motion of a solid through a liquid, on vortex motion, on viscous liquids, and on the high-speed motion of a gas. The fundamental formulation of most of the subject-matter is concentrated in one chapter only, of which the author says in his preface that in it " the general properties of fluid motion continuity, dynamical equation, pressure, energy, and vorticity are studied in the light of the vector formulation whose advantage is then clearly seen ". There are numerous ' examples ' at the end of each chapter. This edition differs from the first by changes in presentation, by the introduction of general methods of writing down formulae for the disturbance of a given unbounded potential flow by a circular cylinder (two-dimensional motion) or by a sphere, and by the addition of a chapter on high-speed gas flow.

When all that has been said, it remains that the strength of the book is as a textbook for acquiring facility in the use of vector calculus and the elementary theory of the complex variable.

I have thought it advisable to begin with this rather dull account of the contents of the book, and to stress the matters wherein I think its strength lies, because I believe that a reader who takes its contents as a balanced and satisfactory account of hydrodynamics will be led astray. It is true that it deals with such matters, and in such a way, as are easily taught to mathematical students in our universities, and most of those students prefer this subject-matter to those other things that I shall mention briefly, and prefer this treatment to a deeper, more subtle, more physical presentation. Moreover it is comparatively easy to set examination questions for mathematical students on this subject-matter. To a considerable extent this book, in fact, fits in with, is the result of, and tends to perpetuate, the present situation of the teaching of hydrodynamics in our universities, and it therefore has, I think, become, and will continue to be, a popular textbook. From my belief that an intelligent, well-equipped reader, seeking to know what hydrodynamics is about, would not find in this book a satisfactory and balanced account, it necessarily, and correctly, follows that I would welcome changes in the teaching of hydrodynamics.

As far as I know, very little hydrodynamics, if any, is taught to students of physics or (except in advanced courses on aeronautical engineering) to students of engineering. Valuable courses can be designed for each of these classes. At present, however, it is regarded exclusively as a branch of " Applied Mathematics ". Whether it be, at any rate partly, due to its practically complete separation from physics or not I cannot say, but it certainly seems that much of excellent educational value and real interest is lost by present teaching methods, which fit in with a book such as the one under consideration.

This is not the place to go into detail about suggested changes of matter and manner; some further remarks, however, are required, as at any rate a partial explanation of what has been written above.

Roughly speaking, hydrodynamics may be taught as a branch of theoretical physics, a branch of experimental physics, and a field for the application of mathematical techniques. In any course the three kinds of ingredient must be mixed, the methods of presentation and the ratios of the ingredients varying with the type of audience (or reader).

Hydrodynamics is an excellent introduction (after a first course on mechanics) to theoretical physics. The primary aim must be to stimulate the student to think physically, with

imagination, and in detail, about the processes and phenomena involved, and to learn to translate such a detailed physical understanding, when achieved, into mathematical language. The course would begin with a thorough exploration, along these lines, of the kinematics of the motion of a continuous medium : such things as continuity, convective rates of change, flux through a moving surface and its convective rate of change, rate-of-strain, and vorticity, would all be treated at length. The ' Langrangian ' method of mathematical expression would certainly be introduced, as well as the Eulerian, in spite of the fact that it is not used for the solution of problems. Vorticity would certainly be dealt with at length, but even the ' equation of continuity ' is not to be lightly or rapidly dismissed, since the physical notion of continuity should be made explicit, as well as that of conservation of mass. To make clear and explicit the notion of (physical) continuity and its mathematical expression is, in fact, probably the first lesson in theoretical physical thinking. For example, in the derivation of the equation of continuity in the Lagrangian notation, if a fluid particle is at (a, b, c) at time t_0 and at (x, y, z) at a later time t, and if ρ_0 is the density at (a, b, c) at time t_0, ρ the density at (x, y, z) at time t, conservation of mass gives at once that

$$\iiint \rho_0 \, da \, db \, dc = \iiint \rho \, dx \, dy \, dz,$$

where the integrals are over ' corresponding ' regions of the (x, y, z) and (a, b, c) spaces; but (dividing stream lines being excluded from the regions considered for simplicity of exposition) it is the assumed physical properties of the medium that ensure the satisfaction of the mathematical conditions for the application of the theorem on the transformation of integrals,

$$\iiint \rho \, dx \, dy \, dz = \iiint \rho \left| \frac{\partial(x, y, z)}{\partial(a, b, c)} \right| da \, db \, dc,$$

and ensure also that there is a (1, 1) correspondence between points of the two spaces, so that the Jacobian never vanishes; since it is unity at $t = t_0$, it is positive; the modulus signs may therefore be removed. It should be emphasized that this is only a necessarily brief, and rather trivial, example, not expressed with great precision, of a whole point of view. (The Lagrangian method of mathematical expression is not mentioned in the book under review.)

When we come to 'ideal' fluids we have to compromise between emphasizing the tentative nature of the whole enquiry, and undermining the confidence of the student in its value. Certainly, however, in a fluid devoid of viscosity and conductivity, we may not use an argument from molecular structure to justify the assumption of (mathematical) continuity of the velocity derivatives, and we have no other direct argument left; we can only regard the whole process as purely tentative, or introduce an idealization of what is known from observation and theory, of the motion of real viscous fluids. Vortex sheets at least should surely be introduced from the beginning—so we may as well have the boundary condition of no slip satisfied by the introduction of vortex sheets coincident with solid bounding surfaces. Such complications at this stage make more advanced understanding much easier. After these matters have been explained, Kelvin's circulation theorem, properly obtained and explained, is the keystone of the whole structure; the direct deduction therefrom, however, of Helmholtz's important theorems on the vorticity is probably insufficient, being too subtle, for the average student; and the most convincing deduction is from Cauchy's equations for the vorticity (again in the ' Lagrangian ' notation), which are easily found by a transformation of the integral form of the circulation theorem. Since Helmholtz's equations are, with extended mathematical conditions, equivalent to the differential form of the circulation theorem, Cauchy's equations may be presented as the integrated form of Helmholtz's equations.

Some attention must be paid, at all stages, to sufficient mathematical conditions, where these are (as they often are) of physical interest and importance; but a prolonged insistence on anything approaching the minimum conditions necessarily becomes too tiresome for a first course, even for mathematicians; compromise is necessary.

It is, then, in the presentation of the foundations of the subject that this book, and most current teaching, seems weak. The subject is presented as easy, and in such a way that its value as a training for the theoretical physicist is small; in fact, it is difficult and subtle, and an excellent training. Some of the accepted methods of presentation are wrong or misleading; much is correct, but presented in a very uncritical manner. In this connection, my attention has lately been drawn again to the following relevant passage from J. S. Mill's *On Liberty of Thought and Discussion:* " Thirdly, even if the received opinion be not only

true, but the whole truth, unless it is suffered to be, and actually is, vigorously and earnestly contested, it will, by most of those who receive it, be held in the manner of a prejudice, with little comprehension or feeling of its rational grounds. And not only this, but, fourthly, the meaning of the doctrine itself will be in danger of being lost, or enfeebled, and deprived of its vital effect on the character and conduct: the dogma becoming a mere formal profession, inefficacious for good, but cumbering the ground, and preventing the growth of any real and heartfelt conviction from reason and personal experience."

In addition to this, most important, matter of the presentation of the foundations of the subject, two other general criticisms may be made. In a work on theoretical hydrodynamics no discussion is to be expected of experimental technique, but the student might reasonably expect to be guided towards an ability to form reliable judgments on when, and in which parts of the field, the results of his calculations approximately agree with observation in real fluids, and when they violently disagree. No such guidance is attempted; the two pages in the opening chapter are quite inadequate, and are, in any case, not referred to again; the general impression that a student calculating the " flow over a ditch or mound " or " the flow past a cylindrical log " (p. 167 *et seq.*), for example, will acquire is most probably the quite incorrect one that his calculated flow bears at least a close resemblance to an actual state of affairs. Another point, which may be rather more a matter of opinion, is that when much space is devoted to the application of mathematical techniques to the calculation of potential flows (as it may legitimately be in an *extended* course for mathematicians and engineers), then surely it is advisable to spare a little space to discuss the computation of flows past other than ' simple ' shapes; important and elegant as such ' simple ' calculations are, some recognition might be given to the fact that the man-made world is not populated, wholly or mainly, by spheres and ellipsoids, circular and elliptic cylinders and Joukowski aerofoils, and their very near relations.

It would be out of place to look for mathematical rigour in a book of this nature, but there are two places where more care would seem advisable. After it has been proved that the velocity potential ϕ tends to a constant C at infinity, some mention of the orders of $\phi - C$ and grad ϕ at infinity seems necessary before it is asserted, in considering the kinetic energy of an infinite liquid (p. 92), that the limit of the integral of $(\phi - C)\partial\phi/\partial n$ over an infinitely large surface is zero. (A similar remark really applies to the discussion of D'Alembert's paradox for an unbounded liquid, but this discussion is in the ' introductory ' chapter.) A more important example of lack of care is on p. 79. The following sentence occurs : " Consider a fluid particle which has no vorticity; from (1), it then follows that $d\boldsymbol{\zeta}/dt = 0$, and therefore the particle never acquires vorticity." (Equation (1) is Helmholtz's equation for the vector vorticity $\boldsymbol{\zeta}$, with uniform density.) The theorem is correct; the ' proof ' is quite fallacious, since it amounts to the assertion that a function $f(t)$ of t is identically zero if $df/dt = 0$ whenever $f = 0$, which is certainly not necessarily true (cf. $1 - \cos t$). The same error occurs in a more indirect form in the consideration of Helmholtz's theorem in the next section. This error has a long history; it appears that Helmholtz himself deduced his theorem in this defective manner; criticism of this kind of proof of Lagrange's velocity-potential theorem was made by Stokes, to whose writings the attention of Lamb was drawn by Larmor. (For references, see Chapter VII of Lamb's *Hydrodynamics*.) The error can be corrected, but proofs from Kelvin's circulation theorem, and from Cauchy's equations, are well worth setting out.

There are a few other places where a student may be seriously misled. Except for zero pressure gradient, equation (6), the momentum equation for the boundary layer, on p. 537, is wrong; in the multiplier of the pressure gradient the boundary-layer thickness should be replaced by the displacement thickness, i.e. the term $-(h/\rho)(\partial p/\partial x)$ should be

$$-\frac{1}{\rho}\frac{\partial p}{\partial x}\int_0^h \left(1 - \frac{u}{U}\right) dy.$$

The error arises from a previous neglect of dU/dx. In the discussion of the hodograph method for high-speed gas flows, it is rather misleading to state (p. 561) that the streamline through the cusp of a limit line may be taken as a solid boundary, since this streamline has infinite curvature at such a cusp. Also (p. 562) it is the square of the Mach number M, and not M itself, that is equal to $2\beta\tau/(1-\tau)$, so the numerical values given are for $M^2_{\max}$.

It is proper that in closing this review I should again draw the attention of any reader of it to the opening remarks on the strength and value of the book. SYDNEY GOLDSTEIN.

Theory of Atomic Collisions, by N. F. MOTT and H. S. W. MASSEY. Pp. xv + 388. 2nd Edition. (Oxford: University Press, 1949.) 35*s*.

In recent years, the study of collisions between atomic particles has received strong impulses from the development of nuclear physics and from the investigation of the various kinds of elementary particles newly discovered in cosmic radiation. On the one hand, the peculiar short-range interactions of nucleons give rise to characteristic scattering effects, whose theoretical analysis is of the greatest importance for the study of the properties of these interactions. On the other hand, the phenomena accompanying the passage of particles through matter, so fundamental for the techniques used in nuclear and cosmic-ray physics, have led to a considerable development of the discussion of the different collision processes between particles and atomic or molecular systems involved in these phenomena.

The second edition of Mott and Massey's classical treatise reflects this shift of emphasis on problems connected with nuclear physics. The authors have wisely decided, however, to confine themselves to the more fundamental aspects of the theory of nuclear collisions, to which a whole chapter and a number of sections of other chapters are devoted. Everything that concerns the detailed treatment of atomic and molecular collisions has been omitted in the present edition, and another volume (by Massey and Burhop) is announced, in which these topics will be more adequately dealt with.

It is superfluous to praise a book which has long since asserted itself as an indispensable auxiliary to all atomic physicists, but a few words about the new sections on nuclear collisions will not be out of place. The treatment, which does not aim at being exhaustive, is truly admirable both by the clever selection of the topics of most importance and of the illustrative examples, and by the clarity of the exposition. The only notable omission is that of Schwinger's method of the 'effective range', which presumably appeared too late for inclusion. I must confess a slight disappointment in seeing that even such consummate experts as our authors have apparently been baffled by the difficulties of the nuclear 'dispersion theory'. It is true that (according to some as yet unpublished investigations by Dr. Humblet) a satisfactory theory would seem to require the help of some high-brow and little-known mathematics. As it is, the treatment given in this book, in spite of its admitted lack of rigour, is certainly a very clear introduction to a difficult subject.

In conclusion, the authors may be congratulated for having so brilliantly upheld the high standard set by the previous edition of their work, and again ensured that future generations of physicists will be indebted to them. L. ROSENFELD.

The Nature of Physical Reality: A Philosophy of Modern Physics, by HENRY MARGENAU. Pp. xiii + 479. (New York: McGraw-Hill, 1950). $6.50.

The author's main object in writing this book has been to show that "men engaged in the development of physical theory can profit from philosophical reflection about the meaning of their research", and should not be content with those attitudes of "uncritical realism, unadorned operationalism, and radical empiricism, which pervade . . . much of the thinking on subjects of science". He obviously hopes that his book will become a standard textbook, and at the end of each chapter he has provided a useful bibliography for further reading. Unfortunately, in this country (at least) it is most unlikely that the author's object will be achieved, as the book is far too expensive. This is unfortunate, for despite some infelicities of style and a tendency to wordiness, Professor Margenau has many sensible things to say and his insight is often illuminating. Whatever one's opinion may be about the book as a whole, it is certainly a most welcome sign that the professor of natural philosophy and physics at Yale should seek to emulate his famous opposite number at Harvard (P. W. Bridgman) in directing the attention of physicists to problems of philosophy of science.

The book begins with six general philosophical chapters concerning science in its relation to 'reality', followed by chapters on space and time, mechanics, continuous media, thermodynamics, probability and statistical mechanics. After a short chapter on the general picture thus suggested of the (macroscopic) physical world, three chapters follow on the basic ideas of quantum physics. The author concludes with chapters on causality and the exclusion principle, and a final summing-up in which he discusses the scope of 'physical reality' and its relation to other modes of 'reality'.

The central theme of the book is expressed in the author's statement (p. 73) that 'Experience moves from data to constructs via guiding relations which are called "rules of correspondence"'. The author points out in some detail that data alone cannot furnish sufficiently stringent conditions to render our understanding of nature unique. In his discussion of the views of previous philosophers of science, he shows how Poincaré regarded the selection of the mental constructs required to discipline our intuitions and to bring order into data as being largely a matter of *convention*, whereas Mach regarded such constructs as *fictions*, invented for 'economy of thought'. The author ,however, like the great American philosopher of empiricism Charles Pierce, believes that a law of nature is something which demands a reason, and that the truly fundamental laws are not merely correlational but go deeper. He asks : what are the principles which supplement the rules of correspondence in their function of producing acceptable constructs? In a most illuminating discussion of the history of the theories of gravitation (p. 170) he remarks that "Although few would admit it, there is an admixture of anthropomorphism in most judgments regarding what constitutes an explanation". With regard to the principles guiding us in the construction of theories in general, he argues cogently that "they first emerge in the stream of experience as tentative expedients, grow into implicit beliefs with increasing application, and finally, strengthened by repeated success, pervade the entire texture of our theories about the world. Their ubiquity makes them extremely difficult to detect, and indeed leads many positivists to deny their presence altogether".

G. J. WHITROW.

Beiträge zum neuzeitlichen Weldbild der Physik: *Das Plancksche Wirkungsquantum*, by P. JORDAN; *Dialektischer Materialismus und theoretische Physik*, by K. ZWEILING. Pp. 54. (Berlin : Akademie-Verlag, 1950.) No price.

Under a somewhat funereal black cover with white lettering two essays are brought together which are so different in outlook and purpose that one wonders at the motives (if any) for such a queer assemblage. Professor Jordan's share is a very readable account, in a condensed but easily understandable form, of the fundamental ideas underlying quantum theory. It is written in a terse and lucid style and brings out beautifully all essential points. As regards the epistemological problems raised by the interpretation of the theory, Jordan shows himself a faithful disciple of Bohr : he writes throughout *im Kopenhagener Geist*. Apart from a discrete allusion to his old favourite Hume, he rightly dismisses all philosophical juggles about causality and contents himself with a matter-of-fact description of the statistical character of quantal laws.

The very sobriety and directness of Jordan's excellent essay enhances the contrast with the other author's pretentious and intemperate chatter. If this was just another of the usual productions of the idealistic school of thought, I would leave it at that. But as it purports to discuss the impact of Marxist ideas on theoretical physics, I feel that in view of the fundamental significance of these ideas for the future development of society and science, a word of protest and warning is needed against such a complete misrepresentation of them. What we have here has in fact nothing to do either with Marxism or with theoretical physics : it is just an attempt to squeeze an ill-digested and misunderstood version of the ideas of quantum theory into a kind of dogmatic system derived from Marxism by the same process as mediaeval scholastics was derived from Aristotle's writings.

Abundant quotations show that our author has diligently crammed the *Anti-Dühring*, but somehow he missed the following sentence : "As soon as every single science is required to elucidate its position with respect to the universal relationship between things and to the knowledge of things, any special science of this universal relationship becomes superfluous. What then remains of all previous philosophy is the doctrine of thinking and its laws : formal logics and dialectics. Everything else is embodied in the positive science of nature and history."* It seems to me that this single sentence adequately settles the question of the relations between science and philosophy.

L. ROSENFELD.

*F. Engels, *Herrn Eugen Dührings Umwälzung der Wissenschaft* (Moscow : German edition), 1946, p. 29 (reviewer's translation).

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ABSTRACTS FOR SECTION B

The Cohesion of Alloys: I—Intermetallic Systems formed by Copper, Silver and Gold, and Deviations from Vegard's Law, by M. A. JASWON, W. G. HENRY and G. V. RAYNOR.

ABSTRACT. In order to extend the theory of the cohesion of metals to alloy structures a new treatment is considered. The excess energy of the solid solution, as compared with that of a mixture of the pure components, is estimated by considering that the introduction of a solute atom causes a major disturbance extending only to its nearest neighbours, and a less serious disturbance in the surrounding matrix. For a face-centred cubic structure, therefore, attention is directed to the group of thirteen atoms formed by the solute atom and its twelve symmetrically situated solvent atoms. The size of the atomic polyhedra forming this group is different from the sizes of the polyhedra in the solvent matrix, and the equilibrium size of the polyhedra within the group is calculated from the known lattice energies of the components, the atomic radii of the components, and the strain energy introduced into the matrix, which is a measure of the long-range minor disturbance. For this purpose it is assumed that the variation with volume of the energies of the components in the alloy is the same as in the pure metals. Thus, the excess energy w associated with the group of thirteen atoms is $w=\{12\epsilon_1(r)+\epsilon_2(r)\}-\{12\epsilon_1(r_1)+\epsilon_2(r_2)\}$, where r_1 and r_2 are

the radii of the solvent and solute atoms, and ϵ_1 and ϵ_2 are the cohesive energies of the solvent and solute metals. w may be plotted against r, and the attendant strain energy in the matrix may be similarly plotted. The sum of these energies is minimized to give the equilibrium size of the atomic polyhedra within a group of thirteen atoms. Using these conceptions, the deviations from Vegard's law to be expected in the solid solutions formed by copper, silver and gold taken in pairs are evaluated. The sign of the deviation is correctly predicted in all cases; quantitative agreement between the magnitudes of the expected and observed deviations is obtained for the copper–silver alloys, which provide the most favourable case for treatment. Application of the theory to problems of solid solution formation is briefly discussed. In its present form the theory applies only to dilute solid solutions.

The Cohesion of Alloys: II—Some General Metallurgical Implications, by W. G. Henry, M. A. Jaswon and G. V. Raynor.

ABSTRACT. On the basis of the theory developed in the first paper of this series, certain phenomena of general theoretical interest may be interpreted. The theory indicates that, for cases of mutual solid solubility of the two components of a binary alloy, the wider solution should be formed where the smaller ion is dissolving in the solvent with the larger ion. This is in agreement with observation. The theory also interprets adequately the observation that, in general, the less compressible of a given pair of metals tends, at a given temperature, to dissolve more of the metal with the higher compressibility than the reverse.

The possible effect on solid solubility relationships of the mutual distortion of the electron clouds of the component ions in a binary alloy is also discussed from the point of view of the theory, and it is concluded that such distortion effects are insufficient to account for the difference between the equilibrium diagrams for the copper–gold and copper–silver alloys. It is suggested that mutual distortion of the ions is not an important effect for the alloys formed by metals in Group IB of the Periodic Table, taken in pairs. For alloys containing small ions bearing a high charge, however, this factor may still be of importance.

The Cohesion of Alloys: III—Extension to High Solute Concentrations, and Application to the Alloys of Group IA Metals, by W. G. Henry and G. V. Raynor.

ABSTRACT. The theory developed by Jaswon, Henry and Raynor (1951) in the first paper of this series permits an estimate to be made, in dilute solution, of the extra energy Δ_{12} associated with the solution of metal 2 in metal 1 to form an alloy. In order to apply this theory to problems of solid solution formation, it is necessary to extend it to cover cases of relatively concentrated solution, when the variation of Δ_{12} with composition must be considered. A reasonable extension is discussed in the present paper, making the assumption that Δ_{12} varies linearly with composition. It is shown that if Δ_{12} is large, limited solid solution formation is to be expected, while if Δ_{12} is small, extensive or complete solid solution formation is possible. Calculations made for the alloys of the alkali metals, taken in pairs, give results in good agreement with experiment, and interpret the fact that solid solution formation is restricted in all the possible systems except K–Rb, K–Cs, and Rb–Cs, for which extensive solid solutions exist.

Further extension of the theory to include the liquid state enables the relative magnitudes of the liquidus depressions in the systems K–Rb, K–Cs, Rb–Cs, Na–K, Na–Rb and Na–Cs to be accounted for, and also interprets the compositions of the eutectic points in the systems Na–K, Na–Rb and Na–Cs. The formation of immiscible liquid systems is also discussed.

The Thermal Conductivity of a Copper–Nickel Alloy at Low Temperatures, by J. K. Hulm.

ABSTRACT. The thermal and electrical conductivities of an alloy of 80% Cu and 20% Ni with average crystal grain size 0·011 mm. have been measured at liquid hydrogen and liquid helium temperatures. A comparison of the results with Makinson's theory suggests that the thermal conductivity between 2° K. and 20° K. is the sum of a temperature proportional term due to electron transport with impurity scattering and a T^2 proportional term due to lattice wave transport with electron scattering, both terms being of the same order of magnitude.

Velocities of Steel Fragments after Perforation of Steel Plate, by K. E. SPELLS.

ABSTRACT. Mild steel fragments (right square prisms, 1·593 cm. × 1·593 cm. × 0·711 cm.) were projected normally with velocity 1,469 m/sec. against mild steel plates of thickness between 0·21 cm. and 0·85 cm.; usually impact was with the full square fragment face. Perforation occurred by removal of a plug rather larger than the fragment face, but tending to diminish with plate thickness. Fragment and plug were shattered by the impact, the pieces emerging along somewhat divergent paths. Velocities were measured with a Cooper chronograph, and in general were approximately the same for the principal pieces of fragment and plug. The residual velocity of the principal pieces may be predicted with reasonable accuracy for plate thicknesses up to about 0·5 cm. by assuming momentum to be conserved between the attacking fragment and a plug of equal area. For thicker plates this leads to too high values of the residual velocity, presumably because of the neglect of the motion communicated to the rest of the plate.

Fragments of velocity 900 m/sec. suffered very little breakage against 0·21 cm. plates; residual velocities were not measured.

The mechanism of prenetration is discussed.

An Air-Cored Synchro-Cyclotron for 400 *MeV. Protons*, by L. RIDDIFORD.

ABSTRACT. It is considered that the most reasonable proposition for accelerating protons to very high energies, using an instrument which employs a magnetic field produced by an air-cored coil, is to operate the machine as a synchro-cyclotron. An investigation of the energies available from such accelerators for given amounts of stored magnetic-field energy is carried out on the basis that the limit is set by the mechanical forces exerted on the coil. It is shown that the power requirements are comparable with those of large iron-cored accelerators at present under construction. In a machine with a useful orbit of radius 11·8 cm., it is possible to provide a field of $2{\cdot}7 \times 10^5$ gauss over the circle enclosed by that orbit, so that protons would be accelerated to an energy of 400 MEV.

Interferometric Studies on the Vibration of Piezoelectric Quartz Plates, by S. TOLANSKY and W. BARDSLEY.

ABSTRACT. A description is given of the application of a number of multiple-beam interference methods to the study of the piezoelectric oscillations of some quartz crystals. The distribution of surface nodes and anti-nodes of motion and the amplitudes of oscillation are revealed by simple methods. By employing a stroboscopic illumination technique the phase relations between the various vibrating regions of the crystal suface are revealed. The nodal regions are shown to be at rest to within less than 50 A. and the surface deformations are revealed to at least a similar order of accuracy. By a modified technique fringes are obtained through the crystal body and these reveal changes in the optical thickness. One crystal developed sharp surface discontinuities after being set into oscillation, indicating that crystallographic glide or slip had taken place. This is shown to be closely related to the familiar shattering of quartz crystals at excessive amplitudes of oscillation.

On the Spherical Aberration of Electron Emission Systems, by O. KLEMPERER and Y. KLINGER.

ABSTRACT. Spherical aberration coefficient and source diameter have been measured for a ' hairpin ' emission system. Both have been found to be smaller than the corresponding values of various other emission systems.

Investigation of Electron Optical Properties of an Electrostatic Focusing System, by W. E. SPEAR.

ABSTRACT. It is shown that the combination of paraxial ray tracing and a dynamical determination of the electron trajectories in the cathode region leads to a complete analysis of electron-optical immersion systems, once the potential distribution is known. The method is applied to an electrode arrangement recently described for use in a fine focus X-ray tube. In particular it is shown that a demagnified image of the emitting area of the hairpin filament is produced close to the anode, if the outer electrode of the system is at cathode potential. A magnified image is formed near the emitter if this electrode is at anode potential. The results are in good agreement with experiment. A discussion of aberration and crossover is included.

Electron-Optical Systems with Helical Axis, by D. GABOR.

ABSTRACT. As the chromatic error of focus has the same sign in all electron lenses with straight axis, achromatic combinations do not exist. It is shown, however, that systems with curved axes can be designed which are equivalent to centred systems in the gaussian approximation, but have chromatic error of opposite sign, and thus may be useful as correcting elements. Systems with a helical axis, with a helical electrostatic field so shaped as to eliminate first-order astigmatism, have particular advantages. In such systems images of unit magnification are produced at equal intervals along the helical axis. Under certain conditions the transverse chromatic shift can be made zero in every second, or third, . . . image, while the longitudinal error of focus can be given any negative value by suitable choice of the pitch. Such systems may find application in secondary emission and dark-field electron microscopes, and particularly in diffraction microscopy.

At a certain pitch the chromatic error becomes infinite. This system is particularly easily realized by means of two coaxial cylindrical electrodes. It is useless as a chromatic corrector, but may find applications as a velocity spectrograph.

An Investigation of certain Properties of the Ionosphere by Means of a Rapid Frequency-Change Experiment, by B. H. BRIGGS.

ABSTRACT. The paper is concerned with the recording of various characteristics of a radio wave reflected from the ionosphere as the frequency is altered rapidly.

An apparatus is described in which a receiver is kept in tune with a sender by means of automatic frequency control circuits operated by the direct pulse from the sender. The tuning is corrected by each pulse and remains fixed for the time between pulses. A frequency range of 1 Mc/s. can be covered in 1 sec. and may be selected anywhere in the range 2–20 Mc/s.

A number of applications of the apparatus are described and typical records are reproduced. The irregularities of ionization present in the normal regions are investigated by the observation of the irregular variations of the amplitude of the reflected wave which are produced when the frequency is altered. Irregularities of ionization are sometimes found to be localized in height. Observations of the reflection coefficient of the abnormal region E suggest that there are two distinct types of region, one an irregular region consisting of scattering clouds, the other a coherent layer with a thickness of the order of 5 km. The apparatus is also used to study the behaviour of the subsidiary critical frequencies often present below the main critical frequency of region E. It is found that these are always decreasing in critical frequency whenever they are observed. Records of amplitude and group path near the critical frequency of a region can be used to determine the collision frequencies of electrons. The treatment is mainly descriptive, and a full discussion of those records which require a detailed quantitative analysis is reserved for a later paper.

Ag (epitaxial) on NaCl (110).

Figure 1. [1$\bar{1}$0] azimuth.

Figure 2. [001] azimuth.

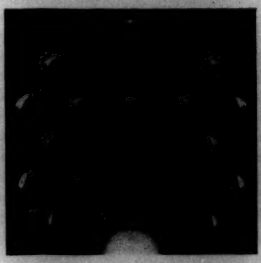

Figure 3. [1$\bar{1}$0] azimuth.

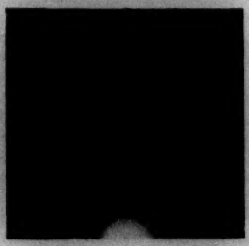

Figure 4. [001] azimuth.

Ag (epitaxial) on NaCl (111).

Figure 5. [11$\bar{2}$] azimuth.

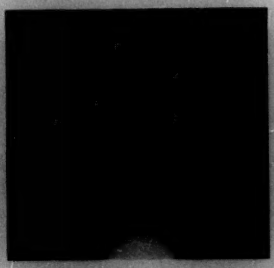

Figure 6. [1$\bar{1}$0] azimuth.